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XXIII CICLO

NOVEL FLEXIBLE PVC COMPOUNDS CHARACTERIZED BY IMPROVED SUSTAINABILITY AND REDUCED PLASTICIZER MIGRATION

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Summary

The present work stems from a collaboration with the company Faraplan SpA. Faraplan which belongs to the group Fitt SpA appears competitive in the globally production and processing of polymers. Faraplan SpA, UNI EN ISO 9001:2000 certified company, is a leader in rigid PVC pipes design and manufacture, corrugated HDPE, PE film, PVC gutters, PVC granules, products for construction and hydraulic sectors.

The laboratory, however, not only covers these areas of interest, but deals with all the other competences of the group's activities ranging from PVC and PE injection molding and a whole catalog of flexible PVC pipes for different applications (transport liquids, gases, food contact, high pressure, garden, etc. ..).

The subject of this study is the spiral pipe. This is a tube made of a rigid PVC spiral, with structural purposes, covered by flexible PVC one. These tubes, as well as many other products, must be in compliance with international standard parameters (UNI EN ISO 3994) that establish the characteristics of the final product and the tests to overcome to be considered by law.

Some of these products do not exceed a particular durability test: the "Reinforcement Fracture Test". It plans to cut the pipe into parts (containing at least three full coils of rigid PVC) and cut them again, longitudinally, separating the coils so as to create specimens with a C shape (figure 1). The pipe sections are placed and left for several days on suitable blocks of size W (depending on the tube diameter) that hold them open (figure 1). The simplest test requires that, after 14 days, the specimen shall withstand the bending on itself without showing cracks or break. In the typical test instead the specimens must overstay four months on the blocks.

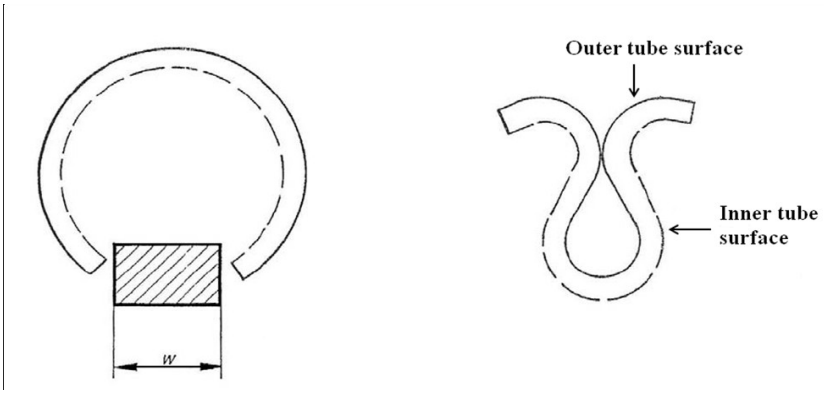


Figure 1: Schematic representation of reinforcement fracture test, W is the thickness of the block.

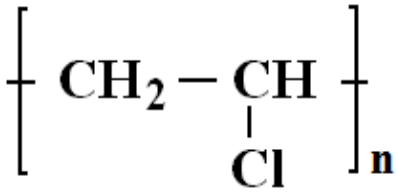
The reason why this test fails is due to the plasticizer migration from flexible part toward rigid one. The topic of this study is to investigate different approaches aimed to reduce the plasticizer migration and create a back-ground of knowledge in order to adjust and optimize all the PVC products.

Chapter 1

The polyvinyl chloride (PVC)

1.1 The polyvinyl chloride

Polyvinyl chloride, commonly abbreviated PVC, is a thermoplastic polymer with a linear structure similar to polyethylene having one of its hydrogens replaced with a chloride atom:



Chemical formula of polyvinyl chloride (PVC)

The presence of a chlorine atoms confer to the monomer its distinctive characteristics being also responsible for the polymer degradation by the production of hydrochloric acid (HCl). Polyvinylchloride is generally transparent with a bluish tint. It is attacked by many organic solvents but it has a very good resistance to oils and it has a low permeability to gases.

The material is characterized by a very wide range of properties which explain its use in many applications. However, in order to achieve all this properties, PVC requires additives during the manufacturing process.

The additives which may be loaded to the polymer are numerous and are distinguished by characteristics which provide to the material. PVC itself is hard and rigid but the addition of plasticizers makes it soft and flexible. Plasticizer plays a major role because, with its addition, it is possible to justify a new definition, that of plasticized PVC or flexible PVC.

It is possible to define rigid PVC and plasticized PVC on the basis of specific rules:

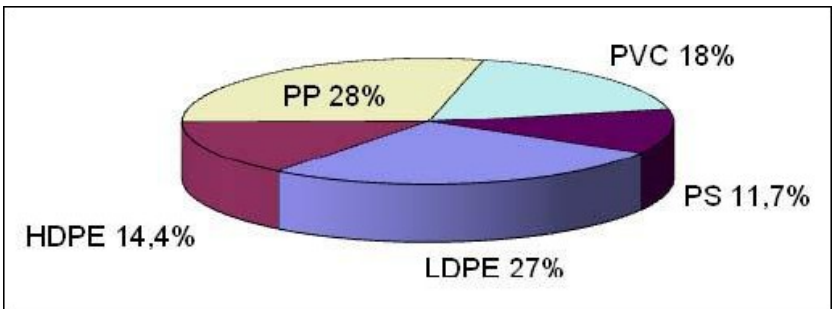
- " Rigid vinyl chloride compound (uPVC) " ISO 1163/1-1980 (E): compound based on vinyl chloride homopolymer or copolymer with at least 50% of vinyl chloride, or other polymers mixture in which polyvinyl chloride is the main component. These compounds may also contain fillers, colors and possibly small amounts of other ingredients to facilitate the workability as stabilizers and lubricants.
- " Plasticized vinyl chloride compound (pPVC) " ISO 2898/1-1980 (E): compound based on vinyl chloride homopolymer or copolymer with at least 50% of vinyl chloride, or other polymers mixture in which polyvinyl chloride is the main component. These

compounds contain a plasticizer and may also contain fillers, colors and possibly small amounts of other ingredients to facilitate the workability as stabilizers and lubricants.

These definitions, other than identify more clearly the exact nature of the material, they also insert two acronyms, that we will use in this thesis: uPVC = rigid PVC and pPVC = plasticised PVC

1.2 The PVC market

The worldwide and national plastics market is ever-growing. In Italy the thermoplastics market is divided as follows:



Thermoplastics market in Italy

The polyvinyl chloride (PVC) is one of the most commercial thermoplastic used in a variety of applications, after polyethylene it is the second most popular plastic for the production of consumer goods. PVC is generally known to have the advantages of low ingredient cost, wide processing versatility, it is used to manufacture various types of products ranging from highly rigid to very flexible.

It is a low-cost plastic which became completely pervasive in modern society. uPVC is employed (for about 70%) for the production of rigid articles such as sheets, tubes and profiles for different applications in industries ranging from construction to transport, packaging furnishings. pPVC is used in the field of electrical wiring and telecommunications and for medical and automotive products.

The increasing use of PVC is attributed to its ability to be a good alternative to other traditional materials such as glass, metals, wood and other plastics. The origin of its success can be ascribed

to the relatively monomer low cost, the uncommon chemical resistance and the ability to be mixed with a large number of additives designed to achieve significantly different physical and mechanical properties.

1.3 PVC polymerization

Polyvinyl chloride is produced by polymerization of the vinyl chloride monomer (VCM). There are four kinds of VCM radical polymerization methods used for the PVC production namely bulk, suspension, emulsion and solution polymerization [1-3]. A comparison of the different VCM radical polymerization methods is shown in table 1. By far the most widely used production process is suspension polymerization.

The manufacturing process consists of two phases: production of the starting monomer (VCM) and polymerization of VCM.

Factor	**Polymerization method**			
	Bulk	Solution	Emulsion	Suspension
Initiator solubility	Soluble in VCM	Soluble in VCM	Insoluble in VCM	Soluble in VCM
Additive	None	Solvent	Water, emulsifier	Water, dispersing agent
Stirring	Not necessary	Not necessary	Necessary	Necessary
Temperature control	Difficult	Possible	Easy	Easy
Isolation of PVC	Recover of VCM	Removal of solvent	Removal of emulsifier	Removal of dispersing agent
Particle size of PVC (μm),	60–300	< 0.1	0.1	20–300

Table 1. Comparison of radical polymerization methods of VCM

Since the vinyl chloride monomer is a colorless gas with anesthetic properties its production and processing is a closed system process where there is a total recycling and washing of the whole thing that comes into contact with suspicious substances, including air. The plants are naturally equipped with automatic monitoring instruments, alerting and blocking of the production cycle, designed to keep all the process conditions in the correct operating range and therefore security.

Polymerization reaction is batchwise operation, started by feeding raw material into the reactor and finished by discharging PVC slurry after polymerization.

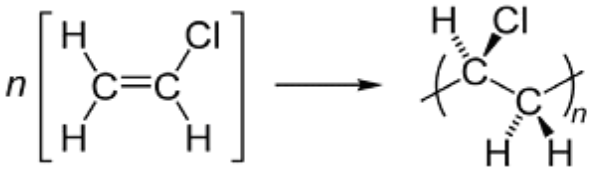
Into the reactor, equipped with cooling jacket and agitator, pure (de-mineralized) water, VCM and protective colloid (suspending agent) are loaded. In this way VCM is dispersed into water by agitation. The reactor is warmed up to a certain temperature and by adding initiator (polymerization catalyst) the radical polymerization of VCM is started. Then the reaction pressure goes down and the polymerization reaction is stopped. After discharge of PVC slurry the reactor is rinsed and the remaining VCM is recovered. The PVC slurry is dried out and transferred to the product silo. Recovered VCM is purified and liquefied by compression and returned to the feed line. In normal operations, the resulting PVC has a VCM content of less than 1 part per million. The product of the polymerization process is unmodified PVC.

Before PVC can be made into final products, it almost always requires conversion into a compound by the incorporation of additives.

1.4 The K value

PVC homopolymer, as well as for all polymers, by definition consists of a chemical structure called unit, which is repetitive for a number of times.

The PVC unit is schematically shown as follows:



The index **n** means the number of times that this structure is repeated, in the case of PVC this value can vary between 500 and 1,500. This results in very long molecules with molecular weights between 31,000 and 94,000.

With regard to PVC there is a fundamental parameter which characterize one resin rather than another: the Fikentscher K value. This K depends on the viscosity ratio η/η_0 of a solution of PVC in cyclohexane (0.5% by weight) at 25 °C as defined by DIN 53726-1983 rule. The empirical relationship linking K to viscosity ratio is:

$$\ln\left(\frac{\eta}{\eta_{\cdot}}\right) = \frac{cK}{1000}\left(\frac{75K}{1.5cK+1000}+1\right)$$

The concept of K was introduced by H. Fikentscher as a molecular weight index of cellulose polymers and it is an indirect expression of the chains polymer average length.

This k value can be evaluated by means of osmometric measurements or steric exclusion chromatography, but commonly it is obtained by means of viscosimetric measures.

Many PVC manufacturers, especially in Europe, instead of providing the polymer molecular weight they prefer to express it by means of K value.

The relationship between K and molecular weights is shown in figure 2.

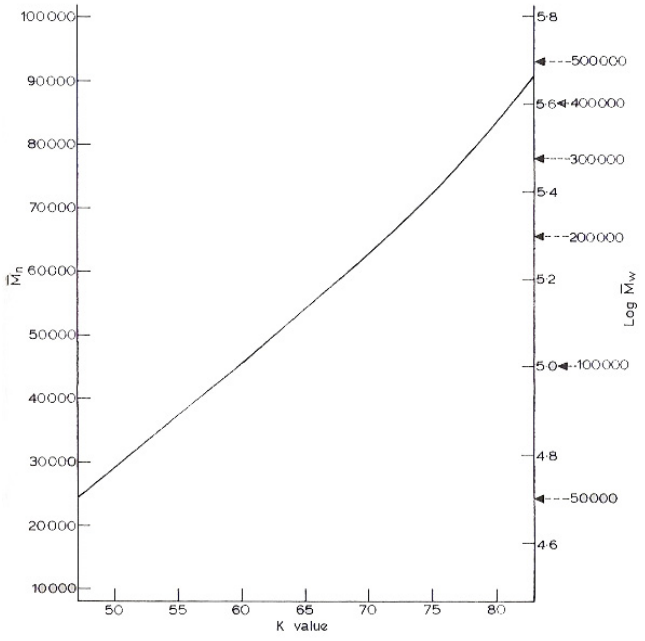


Figure 2. The relationship between the K value and the molecular weight (M_w).

The polymer K value must be chosen according to the type of applications and the final material properties required (table 2). Low K values indicate low viscosity, that is an ideal condition for filling the molds in the case of injection molding.

K value	Type of applications
50<K<60	Injection Molding
60<K<64	Compound for profiles and windows
64<K<67	Tubes and profiles with high mechanical resistance
67<K<100	Flexible PVC
K=100	Indicates a not more measurable index

Table 2. K value in function of the types of application.

1.5 PVC degradation

For many years polyvinyl chloride (PVC) has been one of the most important technical polymers. Surprisingly, it has achieved this status despite it is a very unstable polymer at the action of electromagnetic radiation (light), high-energy (radiation gamma) and heat.

Several studies are aimed at understanding how it degrades and how is possible to stabilize it [4, 5]. Yet further improvements are much to be desired, not only with regard to the property of stability but also with respect to how this property is achieved, in terms of the requisite monetary costs, health and environmental considerations, and the effects of thermal stabilization on other useful properties of the resin.

Because of their technological relevance and intrinsic scientific significance, the thermal degradation and stabilization of PVC have been the subjects of much research. Unfortunately, they also have attracted an uncommon amount of mechanistic speculation that frequently has not been informed by a comprehension of well-known chemical facts.

As a result, much of the literature in this field is not only highly confusing, but also grossly misleading, because it implies that much less is known about the subject matter than actually is the case.

1.5.1 Degradation induced by heat

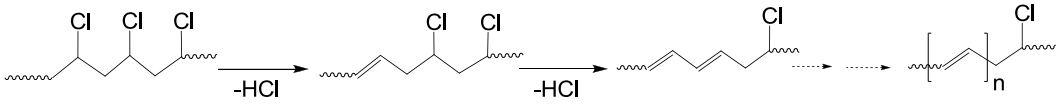
PVC thermal degradation is the result of an autocatalytic process called dehydrochlorination (DHCl). This process is now well-recognized to be a chain reaction in which initiation, propagation, and termination steps occur [6-9].

A very important part of PVC dehydrochlorination is the initial step, which requires a relatively high activation energy. The initiation step leads to the formation of highly reactive "structural defects" [6].

In literature various structural irregularities are discussed as initiation sites of the dehydrochlorination:

1. Chain end groups with initiator residues or unsaturated end groups
2. Branch points with tertiary chlorine atoms
3. Random unsaturation with allylic chlorine atoms
4. Oxidation structures
5. Head-to-head units.

These groups are responsible for the formation of polyene sequences. In fact, during propagation step the thermal degradation process leads to formation of double bonds followed by a so-called rapid zipper-like splitting off of HCl molecules to give polyene sequences [6-9]; see scheme 1. Once they are formed, they can react leading to a cross-linked PVC structure[10].



Scheme 1. PVC dehydrochlorination mechanism. Polyene sequences growth.

Termination step refers to the cessation of polyene growth, which occurs when the polyene sequences still are rather short. In fact, the PVC thermal degradation causes a polyene sequence length distribution wherein the average number of double bonds typically ranging from only about 3 to 20, depending on conditions.

The termination reactions have not been identified. However, several possibilities are apparent, including various intra- or intermolecular cyclizations of the polyenes themselves[6, 11, 12].

The kinetics of dehydrochlorination reaction have been quite extensively studied, but there is lack of agreement on some of the salient features of the mechanism. The mechanisms that occur during degradation are not yet fully understood. There are radical or ionic mechanisms suggested, and the type of reaction depends also on the conditions (temperature, presence of oxygen, etc.) during the decomposition.

Nowadays it is possible to suppress these undesired degradation reactions by: (a) conducting the polymerization process so as to obtain a material with the least amount of imperfections in the chain, (b) seeking to eliminate the HCl gradually formed (seeing that it acts as a catalyst for the dehydrochlorination reaction) by using thermal stabilizers.
On the thermal stabilizers nature and purpose we will discuss in detail in a while.

1.6 Additives

It is now known that virgin PVC does not lend itself to almost any application. The polymer commonly used and sold shows a great variety of uses and it is characterized by countless properties. As already stated, this great expansion and diversification of capacity is due to a large number of formulations that include other additives in addition to the polymer resin.
PVC formulations are designed considering the quantity of components compared with 100 parts of resin, that is, in phr. The content of additives varies widely between different PVC applications, with the main general difference between rigid PVC (uPVC) and flexible PVC (pPVC).
The quantitatively important classes of additives are heat stabilizers, co-thermal stabilizers, plasticizers, helping process (improving the characteristics of the melt and its workability), lubricants and inert fillers, the latter generally added to reduce cost and get more volume for a given amount of polymer. Other classes of additives for specific applications include pigments, impact modifiers, functional agents, flame retardants, UV stabilizers, biocides (to prevent fungal growth on flexible PVC) and antistatic agents.
All rigid PVC based products contain at least a stabilizer and a lubricant. Various other components are incorporated in PVC, sometimes in large quantities with regard to the polymer. Flexible PVC for instance can contain plasticizers up to 80 phr.
The effect of additives on the properties and characteristics of the product is summarized in table 3.
In particular, we will focus only on the nature, the role and the characteristics of the additives employed in our PVC formulations namely heat stabilizers, co-thermal stabilizers and plasticizers.

Additives	Property of PVC article affected
Stabilizer	Prevents decomposition during processing, imparts light or UV radiation and weather resistance
Pigment	Colour, weather resistance
Plasticizer	Improvement of material properties: processability and flexibility
Impact modifier	Impact strength and other mechanical properties
Lubricants	Rheology of the PVC melt, transparency, gloss, surface finish and printability
Fillers	Electrical and mechanical properties
Flame retardants	Burning behavior
Antistatic agents	Electrical properties
Blowing agents	Processing to expanded products

Table 3. Effect of PVC additives on product properties.

Heat Stabilizers

Stabilizers are ingredients that are generally added to PVC in order to prevent thermal degradation and hydrogen chloride evolution during processing leading to improved finished article properties (heat and UV stability).

The most important group of stabilizers are

• metal salts (i.e. calcium and zinc stearates, basic lead sulphate and lead phosphite)

• organo metals (i.e. mono- and diorganotin, tin thioglycolate)

• organo phosphites (i.e. trialkyl-phosphites)

• antioxidants, polyols (i.e. BHT, pentaerythritol)

To reduce PVC degradation, thermal stabilizers are added to the polymer prior to processing.

It is generally accepted that the main roles of such stabilizers are:

(a) To react with the labile chlorine atoms in PVC chain (e.g. allylic chlorine atoms), preventing further dehydrochlorination [13-15], Since these stabilizers are able to reduce long polyenes formation, preventing early resin discoloration, they are called primary stabilizers [13].

(b) To react with HCl generated by the degradation process [13-15] which accelerates PVC thermal degradation [13, 16-18] HCl scavenging does not stop the degradation process completely, but reduces the degradation rate. Because HCl scavengers improve long term stability, but do not protect against short time discoloration (they have little effect on long polyenes formation), they are usually referred to as secondary stabilizers [13].

The main stabilizers used in PVC today are lead compounds, organotin compounds, barium/zinc and calcium/zinc systems. Calcium/zinc stearate are the most "non-toxic" heat stabilizers used in PVC formulations, even though their stabilizing effect is lower compared to the others.

The Ca/Zn stabilizers are obtained from complex mixtures of zinc and calcium soaps with the addition of acid acceptors and organic co-stabilizers.

Co-thermal stabilizers

When possible heat stabilizers should be coupled with co-thermal stabilizer to obtain a synergistic effect improving the heat and light product stability.

Co-thermal stabilizers include various epoxies, phenolic antioxidants, polyols and alkyl/aryl phosphites, which are commonly used to stabilize all the main polymer types.

Epoxies are the most widely-used co-thermal stabilizers for flexible polyvinyl chloride formulations. They are also used as plasticizer, pigment dispersion agents and acid/mercaptan scavenging agents and epoxy reactive diluents. They are obtained by some alkenes oxidation reactions with peracids.

The most common epoxidized oleochemical is ESBO(epoxidized soybean oil) which is an epoxidized glycerol fatty ester. The epoxy functionality provides excellent heat and light stability. In general, it also improves the PVC weathering resistance and it also acts as a lubricant in the PVC formulations.

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Chapter 2

PVC plasticizers

One of the most recent concerns about plastics are plasticizers, the common additives employed in flexible PVC formulations.

The definition of plasticizers adopted by IUPAC in 1951 is still generally accepted: a substance incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability or distensibility. Plasticizers, which are also known as phthalates, make plastics flexible and durable. A plasticizer may reduce the melt viscosity, lower the glass transition temperature (Tg), or lower the elastic modulus of a product.

The plasticizer has to be cost-effective, stable, low in color, compatible with PVC, low in volatility, low in odor, low in toxicity, have good permanence, and must not interact unfavourably with other needed formulating ingredients.

Generally the group of plasticizers is divided into two parts: primary plasticizers and secondary plasticizers. Primary plasticizers are low volatility liquids whose polarity and other characteristics are such that they are sufficiently compatible with PVC not to be readily squeezed out of plasticized PVC. Secondary plasticizers are low volatility liquids whose compatibility with PVC is such that they can be used along with primary plasticizers as part of the plasticizer system.

2.1 Mechanisms of plasticization process

To be effective the plasticizer must be mixed and fully incorporated into the polymer matrix.

To obtain a homogeneous material, from polymer and plasticizer blending, different mixing steps can be defined: plasticizer penetration into PVC particle, plasticizer adsorption and plasticizer diffusion. In the final stage the plasticizer molecules penetrate into the polymer chains groups changing their interaction and softening the matrix.

Different plasticizers will exhibit singular characteristics in the plasticized material, which in turn will be characterized by diverse mechanical and physical properties.

Before discussing the theories that intend to explain this phenomena it is important to point out that the internal structure of plasticized PVC is not homogeneous. In fact, it is possible to distinguish ordered areas with aligned chains, that are not affected by the plasticizer, which interacts with the amorphous structure . The ordered zones, which also exists even though PVC is considered an amorphous polymer, are significant for the final properties of the material. Several theories have been developed to describe the plasticization process.

A significant revision of the theory of plasticization is given by Sears and Darby. In their discussion, the plasticization is described on the basis of three main theories: the theory of lubrication, the gel theory and the free volume theory [1].

According to the theory of lubrication, heating the system, the plasticizer molecules diffuse into the polymer weakening the polymer-polymer interactions (due to the Van der Waals forces). The plasticizer molecules act as screens to reduce the attractive forces between polymer chains preventing the formation of a rigid network. As a result the Tg, in the flexible PVC , is lower allowing a faster polymer chains moving, increasing flexibility, elasticity and elongation.

The gel theory considers the plasticized polymer neither a solid nor a liquid but as an intermediate state held together by a three-dimensional structure governed by weak bonding forces. These bounding forces, between the plasticizer and the polymer, are easily overcome by external strain applied to the material, allowing the plasticized polymer to be bend, stretch, or compress.

The free volume is a measure of internal space available in a polymer matrix. When the free volume increases also the freedom of polymer chains movement increases. A polymer in the glassy state has an internal structure with small free volume consequently the molecules can not move easily, making the material stiff and hard. When small plasticizer molecules are added to the formulation and the polymer is heated above the glass transition temperature, the thermal energy increases and the polymer chains separate themselves creating more free volume. As a consequence the system become more flexible and rubbery.

2.2 Plasticizer efficiency

Plasticizer efficiency may be quantified as a function of PVC Shore A hardness value. Similar comparisons may be made for other mechanical properties, but hardness test reliability and the common practice of a designated room temperature hardness value supports its use to quantify plasticizing efficiency.

Figure 3 graphically represents quantitative determination of plasticizer efficiency, expressed as "Substitution Factor" (SF); in this example , the hardness values of di-isononyl phthalate (DINP) and di-octyl phthalate (DOP) plasticized PVC are compared. It is shown that 80 Shore A hardness is provided by 52.9 phr DOP, while 56.2 phr DINP is required to get the same hardness.

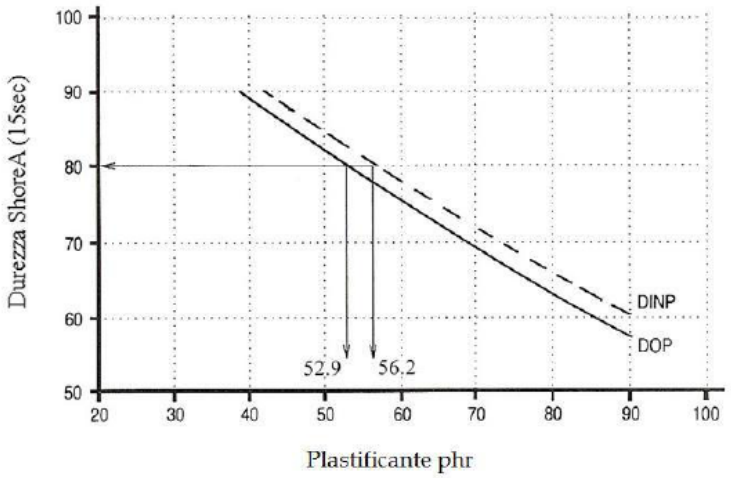


Figure 3. Plasticized polyvinyl chloride Shore A hardness: dependence on the type of plasticizer.

Thus, the substitution factor (SF) for DINP vs. DOP is 1.06, as shown in equation 1:

$$SF = \left(\frac{\text{phr plasticizer at Durometer 80}}{\text{phr DOP at Durometer 80}} \right) = \left(\frac{56.2 \text{ phr DINP}}{52.9} \right) = 1.06 \quad (1)$$

The "SF" indicates that DINP is 6% less efficient than that of DOP. In other words, in order to achieve the same hardness or softness, DINP needs to be added at higher level (6%) compared with that of DOP.

It was found that the SF factor theory is valid for plasticizer levels ranging from 20 to 90phr. A large amount of commercial products and plasticizers have been evaluated so as to classify and regulate the additives properties and performance. All values obtained were always compared with those of DOP, which is taken as a reference.

2.3 Plasticizers classifications

There are several possible classifications justified by variability of the chemical structure, features, range of use and efficiency. It is proper to make a division based on the plasticizers chemical nature namely the functional groups and molecular morphology characterizing the plasticizers themselves. However, in this work, we classify them on the bases of their molecular weight:

- *monomeric plasticizers* which are low molecular weight compounds

- *polymeric plasticizers* which are polymers with higher average molecular weights.

2.4 Monomeric plasticizers

Phthalates, phosphates, trimellitates, citrates, sebacates and adipates are usually used as plasticizers for PVC [2].

The most significant group of PVC plasticizers is phthalate esters: bis(2-ethylhexyl)phthalate (DEHP), di-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di-isodecyl phthalate (DIDP) and di-isononyl phthalate (DINP).

The main exponent of this group is bis(2-ethylhexyl)phthalate (DEHP) commonly called dioctylphthalate (DOP). It is insoluble in water and has a good stability to heat and ultraviolet light, a broad range of compatibility, excellent resistance to hydrolysis and possesses good plasticizing properties. It is an organic compound with the formula $C_6H_4(CO_2C_8H_{17})_2$ (figure 4).

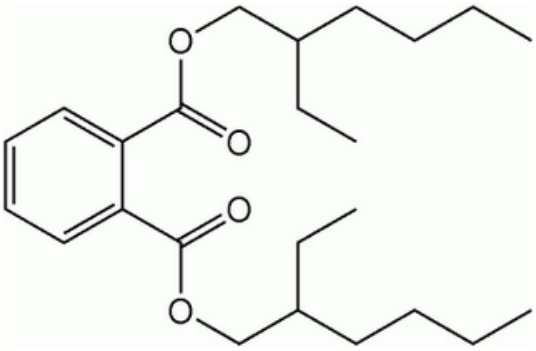


Figure 4. Dioctylphthalate (DOP) structure.

Due to its suitable properties and the low cost, DOP is widely used as a plasticizer in manufacturing of PVC articles [3].

Since they are not chemically bonded with the polymer matrix and because of their low molecular weights, monomeric plasticizers such as DOP have a high tendency to leach out from the polymer [4, 5]. This tendency represent a serious problem as we will discuss in chapter 3.

2.5 Polymeric plasticizers

Polymeric plasticizers are generally used as additives to conventional polymers [6,7]. In PVC applications linear structure polymeric plasticizers are employed as an alternative or in addition to the usual monomeric plasticizers to provide flexibility, softness and lower modulus values and to maintain these characteristics after PVC compound exposure to severe use conditions or harsh environments.

They are commonly used with PVC when permanence is a critical parameter. In fact, because of their higher molecular weight and bulkiness their volatility and diffusivity is reduced compared with monomeric plasticizers. On the other hand, their use usually makes the material more difficult to process [8]. Therefore, a manufacturing dilemma is to select the right molecular weight to use in order to satisfy the conflicting requirements of increased plasticizer retention and decreased manufacturing compatibility and processibility.

PVC has been blended with many different polymers [8-11]. Among them, the most commonly used are saturated polyesters obtained from the reaction between a dicarboxylic acid and a diol [12-15]. Linear saturated polyesters are used in flexible PVC formulations as no migrating alternative plasticizer, since they exhibit good miscibility with PVC. Moreover they are able to improve the PVC mechanical properties, such as abrasion and fatigue resistance.

In the recent years, a growing interest has been shown also for hyper-branched polymers as substitute to phthalate plasticizers for PVC[16-19].

Recently, Choi and Kwak [16] have experimented the use of hyper-branched poly(ε-caprolactone) as plasticizer in PVC. They found that PVC formulations containing hyper-branched poly(ε -caprolactone)s with large number of branches showed excellent migration stability and a plasticization quality as good as the PVC products with DOP.

Lindström and her colleagues used hyper-branched poly(butylene adipate) as migration resistant polymeric plasticizer for PVC [20].

2.6 Hyper-branched polymers

The hyper-branched polymers are a group of materials belonging to the dendritic polymers family, which are recognized as a fourth major class of macromolecular architecture [21]. They represent highly branched globular macromolecules, which can be subdivided, according to their

degree of structural control, into three different categories namely: (a) random hyper-branched polymers, (b) dendrigraft polymers, and (c) dendrimers (see figure 5).

Dendrimers are highly uniform, three-dimensional, monodisperse polymers with a tree-like globular structure and a large number of functional groups. As shown in figure 5, a dendrimer is a symmetrical layered macromolecule which consists of three distinct areas: the polyfunctional central core (dendrimer) or focal point (dendron) which represents the center of symmetry, various well-defined radial-symmetrical layers of repeating units (also called generations), and the end groups.

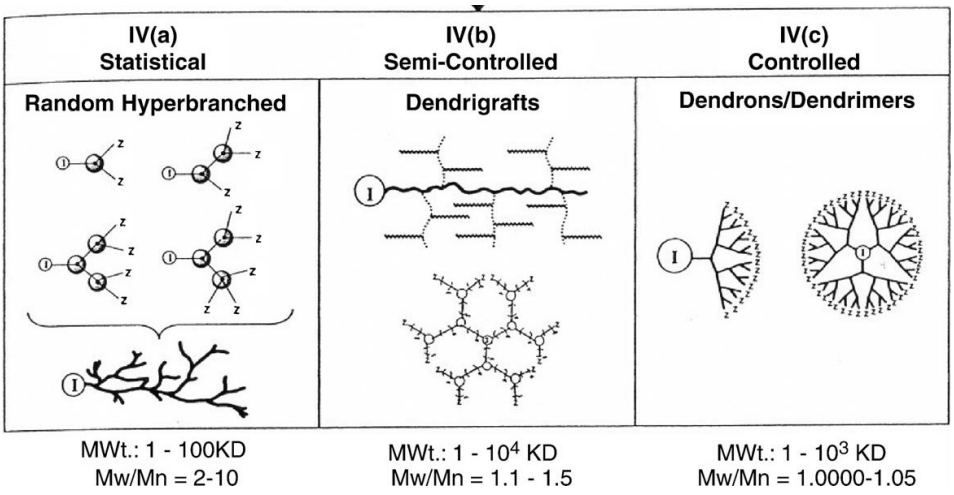


Figure 5. Dendritic polymers: dendrons/dendrimers, dendrigrafts and hyperbranched polymers.

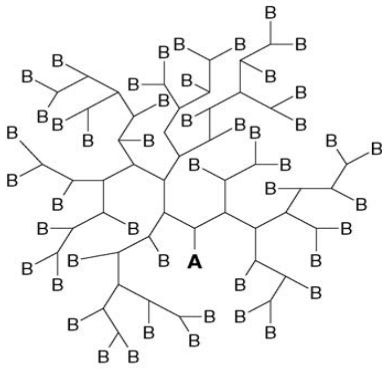
Dendrigraft polymers may be regarded as semi-controlled branched polymer architectures intermediate, in terms of structure control, between dendrimers and hyper-branched polymers [22]. In comparison to dendrimers, dendrigraft polymers are less controlled since grafting may occur along the entire length of each branch generational and the exact branching densities are arbitrary and difficult to control [21].

Hyper-branched polymers (see figure 5) represent another class of globular highly branched macromolecules. According to the increasing number of publications, the interest in these three-dimensional macromolecules complex is growing rapidly. In comparison with analogue linear polymers, their compact structure, the absence of chain entanglements, and presence of a large number of functional end groups enable a spectrum of unusual properties and consequently numerous possible applications.

Unlike conventional linear polymers, hyper-branched polymers do not only show a remarkable selectivity and capacity [23, 24] but, also a comparatively low solution and melt viscosity [25-29] as well as an enormous thermal stability [6, 24] and good compatibility with other materials. Modification of the number and type of hyper-branched polymers functional groups is essential to control their solubility, compatibility, reactivity, adhesion to various surfaces, self-assembly, chemical recognition, and electrochemical and luminescence properties.

As discussed in the literature [30] the variations in many of hyper-branched polymers properties are related to their different degree of branching. It is believed that increasing the degree of branching, a hyper-branched polymer is close to the structure and, consequently, to the properties of a dendrimer.

Nowadays, the shape of a hyper-branched polymer is not fully known, so the representation of such a polymer as a sphere is still considered a mere idealization.



hyperbranched polymers

2.6.1 Synthesis of hyperbranched polymers

Hyper-branched polymers and dendrimers share a few common features such as their preparation from AB*x* monomers leading to highly branched macromolecules with a large number of functional end groups. However, the synthetic approaches for hyper-branched polymers and dendrimers differ substantially.

The dendrimers multi-step synthesis procedures consist of numerous protection, deprotection and purification steps, which have to be applied to ensure good definition of the molecular structure.

Therefore, synthesis of dendrimers is often very expensive and time consuming, and consequently, restrictive for the use in large scale applications.

On the other hand, hyper-branched polymers can be synthesized in one-step polycondenzation of AB_x-monomers ($x \geq 2$) at a reasonable cost, as reported by Stockmayer [31, 32] Flory, [33] Kim and Webster [6].

Although, this simple procedure yields randomly branched polymers with broad molar mass distribution and less perfect globular shape, hyper-branched polymers resemble dendrimers in many physical and chemical properties. The imperfection of their structure originates from the fact that beside fully reacted (dendritic) units, hyper-branched polymers also have some linear units in their structure. Therefore the inner layers of these polymers are usually called pseudo generations. For many applications, where no structural perfection are required, the use of hyper-branched polymers can thus overcome the limitations and restrictions imposed by the complexity of the dendrimers.

A number of excellent reviews on the synthetic approaches for hyper-branched polymers has been published [19, 25, 34-38] giving a detailed insight in the underlying methodologies and reaction mechanisms.

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Chapter 3

Effect of plasticizer migration: Environmental Stress Cracking

3.1 Plasticizer migration

As already discussed poly(vinyl chloride) (PVC) is one of the most heavily plasticized polymers. PVC is able to absorb a large amount of plasticizer giving it wide versatility [1]. However, as stated in section 2.4 because of their low molecular weights, monomeric plasticizers such as phthalates, phosphates, trimellitates, adipates, citrates, etc., have a high tendency to leach out from flexible PVC products into the external environment sometimes directly into animal and human bodies [2, 3].

Recent studies showed that these phthalates have been found in the soil, indoor air, and seawater, indicating that the phthalates endanger the environment and ecosystem [*4-6.*]. Substantial evidence of the toxicity of these plasticizers has been gathered, in particular for members of the phthalate series such as DOP, which is by far the most commonly used plasticizer in flexible PVC applications [7].

Thus the use of phthalate-based plasticizers is being questioned worldwide. For example, the European Commission issued (in 1999) and renewed (in 2003) an emergency ban on the use of six phthalate esters (DEHP, diisononyl phthalate, diisodecyl phthalate, dibutyl phthalate, benzyl butyl phthalate, and di-*n*-octyl phthalate) in toys and childcare articles [8].

In addition, the loss of plasticizers is one of the most dominant adverse factors contributing to aging of flexible PVC [9] making it useless for many applications [10]. Thus, aging has to be slowed down, particularly since aging of polymers increases their brittleness [11], thus causes deterioration of dimensional stability under loads as well as loss of other properties.

The plasticizer migration process can be define as the movement of a plasticizer within and from a PVC compound into or onto a substrate to which it is held in intimate contact. PVC plasticizers can be released from flexible PVC in different ways [12]:

1. Volatilization from the PVC surface to the air.
2. Extraction from PVC to a liquid in contact with it.
3. Migration from PVC to a solid or semi-solid in contact with it.
4. Exudation under pressure.

Additionally, when rigid and flexible PVC are co-extruded, as in the case of Faraplan spiral pipes, if the plasticizer diffusion extent is not controlled or reduced the Environmental Stress Cracking (ESC) phenomena may occur.

3.2 Environmental stress cracking (ESC) phenomena

Environmental stress cracking (ESC) is a solvent-induced failure mode, in which the synergistic effects of the chemical agent and mechanical stresses result in cracking. Plasticizers are recognized as environmental stress cracking (ESC) agents; by adhering to a polymer surface they reduce the surface energy and thus initiate cracking [13, 14]. It is known that materials failure in service can be attributed to the ESC phenomena [14] Lustiger [15] discusses methods of ESC determination for polyethylene to assure a reasonable service life of the material used. Conditions for the use of plasticizers have been discussed by Rabello [16]. Research shows that the exposure of polymers to chemical liquids tends to accelerate the crazing process, initiating crazes at stresses that are much lower than the stress causing crazing in air [17, 18]. The action of either a tensile stress or a corrosive liquid alone would not be enough to cause failure, but in ESC the initiation and growth of a crack is caused by the combined action of the stress and a corrosive environmental liquid. The ESC in polymers involves molecular interactions between the ESC agent and the polymeric material. It causes morphology changes as well as relevant physicochemical phenomena such as stress dissipation, permeation, cavitation, fibrillation, and fracture [19].

3.2.1 Mechanisms of ESC

Polyvinyl chloride compounds rupture prematurely in contact with environmental stress cracking (ESC) agents such as plasticizers. There are a number of opinions on how certain reagents act on polymers under stress. PVC and polymers in general dilate under a stress, increase free volume, and allow diffusion of the ESC agent and plasticization of the polymer [20]. The result is a decrease in the yield stress and glass transition temperature (Tg), as well as a plasticization of the material which leads to crazing at lower stresses and strains [18, 21].

A second view is that the liquid can reduce the energy required to create new surfaces in the polymer by wetting the polymer's surface and hence aid the formation of voids, which is thought to be very important in the early stages of craze formation [21].

Plasticisers leaching from PVC can cause ESC over an extended period of time.

It is understandable that the Environmental Stress Cracking (ESC) phenomena is the reason for which the spiral pipes can not overcome the "Reinforcement fracture test". In these pipes, the

plasticizer migrates from the flexible PVC part towards the rigid one. The pressure applied from plasticizer causes the polymer fibrils breaking generating crazes that rapidly become fractures.

3.3 Reduction of plasticizer migration: Strategies.

A specific tool aimed at reduction of plasticizer migration is *the chemical cross-linking* of PVC [22-24]. Formation of more chemical bonds reduces the free volume and segmental mobility, thus affecting plasticizer diffusion through the matrix. Thus, Romero Tendero et al. used a difunctional amine, namely isophoron diamine (IPDA) as a cross-linking agent for PVC plastisols [22]. In this work, IPDA was used as cross-linking agent for flexible PVC dry blends.

Another option for achieving significant inhibition of plasticizer migration and minimization of property deterioration is blending PVC with a polymeric plasticizer. Necessarily such plasticizers have a reduced ability to migrate compared to conventional non-polymeric plasticizers such as dioctylphthalate (DOP). In this work a linear and hyper-branched polyester were used in PVC formulations namely poly(butylene adipate) and hyper-branched poly(butylene adipate) respectively. The properties of PVC/polymeric plasticizers blends were studied and compared with PVC/DOP (pPVC) formulation.

The last strategy adopted in this work regards the addition of chlorinated polyethylene (CPE) to pPVC formulations. Chlorinated polyethylene (CPE) represent an important class of commercial polymers [25]. CPE resin is mainly used: in blends with other polymers to improve their mechanical properties [26], as compatibilizer in polymer blends [27, 28] as base thermoplastics for extruded, calendered, solution cast and injection-moulded parts and goods.

Nevertheless, in this work CPE was used as a physical tool to create a barrier against DOP migration.

Since the CPE based compounds properties are influenced by the chlorine percentages in polyethylene, the CPE viscosity and the components ratio in the formulations, three different CPEs (having different viscosity and chlorine content) at different amount (7 and 15% by weight) were added in flexible pPVC blends.

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CHAPTER 4

Chemical cross-linking of flexible PVC compound

A specific tool aimed at reduction of plasticizer migration is *the chemical cross-linking* of PVC [1-3]. In this work, IPDA was used as cross-linking agent for flexible PVC dry blends.
In the following the experimental procedure is reported in detail.

4.1 Experimental part

4.1.1 Materials

Rigid PVC sheets were prepared using PVC pellets BENVICVIC® IH007W025AA (Solvay Benvic, Italy). The base polymer used for flexible samples (sPVC) was PVC Lacovyl® S7015 PVC (Arkema, France). (Ca + Zn)-based powder Reapak B-NT/7060 (Ca + Zn 0.5-0.8 phr) (Ca/Zn- Reagens, Italy) and epoxy soybean oil (ESBO- Shangai Yanan Oil and Grease Co.) were selected as heat stabilizer and co-thermal stabilizer, respectively. Low-molecular weight commercial plasticizer dioctylphtalate (DOP) DIPLAST® 0 (purity > 95%) was received from Lonza S.p.A., Italy. The cross-linker IPDA and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and used without further purification.

4.1.2 Sample preparation

Flexible samples prepared were: uncross-linked sPVC (pPVC) and cross-linked sPVC containing 1.2 wt. % (C1), 2.2 wt. % (C2) and 3.2 wt.% (C3) of the cross-linking agent.
The formulations are reported in detail in table 4. Preparation of sPVC-based dry blends was performed in a mechanical blender according to the following procedure.
sPVC and Ca + Zn were preheated up to 60°C and then mixed with ESBO. As soon as the blend reached 80°C, the plasticizer and the cross-linker (when required) were added. Ten minutes mixing time was selected in order to get homogeneous blends. Once the samples reached 100°C, the blends were recovered and then roll-milled in a plasticorder *(*Brabender *model PLE 67152*) at 40 rpm, T = 90°C for 15 min. The flexible sheets were obtained using a hot press (lab-scale Collin P 200 E) at 150°C and 200 bar for 7 min.
Rigid PVC sheets were prepared by press-molding the polymer pellets at 190°C and 200 bar for 7 min.

	Samples			
Components	**pPVC**	**C1**	**C2**	**C3**
sPVC	100 phr	100 phr	100 phr	100 phr
DOP	70 phr	70 phr	70 phr	70 phr
ESBO	2 phr	2 phr	2 phr	2 phr
Ca/Zn	1 phr	1 phr	1 phr	1 phr
IPDA	-	1.2 wt %	2.2 wt %	3.2 wt %

Table 4. Flexible PVC formulations.

4.1.3 Solvent extraction procedure

The efficiency of IPDA as a chemical cross-linker for PVC was evaluated by means of solvent extraction procedure. Soxhlet extraction technique was employed to separate the insoluble cross-linked portion of each flexible sPVC-based samples using THF as solvent at 65°C for 21 h. The extraction thimbles containing the THF-insoluble polymer fractions were then dried by vacuum-pumping in an oven at 100°C for 8 h. The weight percentage (%gel) of gelled flexible sPVC-based portion was calculated gravimetrically according to equation 2 [4]:

$$\%gel = \frac{W_{tg} - W_t - W_i}{W_s - W_i} \times 00 \qquad (2)$$

where W_{tg} = the thimble weight containing the gelled fraction; W_t = the thimble weight; W_s = the sample weight; W_i = the weight of the insoluble additives. In our case W_i = 0 since all the additives were soluble in THF.

4.1.4 Thermogravimetric analysis(TGA)

Thermal stability of flexible sPVC-based samples was evaluated by TGA. Thermogravimetric analysis (TGA) was carried out at 10°C/min heating rate from 25°C to 600 °C under nitrogen flow using a Q5000 (TA Instruments) thermo balance.

4.1.5 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis (DMTA) measurements were carried out using a Triton Technology mod. Tritec 2000 testing machine. Tests were performed in single cantilever bending mode, using a constant frequency of 1 Hz and an oscillation amplitude of 0,01 mm. Samples were heated from -80°C to 40 °C at 5°C/min heating rate. The glass transition temperature (T_g) was taken as the peak temperature of tanδ curve.

4.1.6 Mechanical Properties

The Young's modulus (E), ultimate tensile strength (σ_b), and elongation at break (ε_b) were determined from a traction test by an universal dynamometer INSTRON *mod.*5564 at room temperature using 1 KN load cell, at a crosshead speed of 10 mm/min. The dog bone shaped mini tensile bars were characterized by 2 mm thickness, 4 mm width and 28 mm length.
For each sample a batch of five specimens was tested and the average values were reported.

4.1.7 Migration tests

Small rectangular sheets of flexible sPVC-based samples with approximately 1 mm thickness were placed between two rigid PVC layers with 2 mm thickness and kept under 5.0 kg weight in an oven at 60°C between two glass plates in order to force the migration of plasticizers to the contacting rigid substrates (see figure 6 as explicative setup).

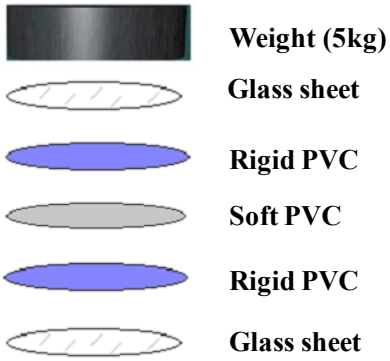


Figure 6. Migration test setup.

Plasticizer migration was determined by monitoring weight increase of rigid PVC. The specimens removed from the oven at different times were immediately weighted. The weight variations were calculated according to equation 3:

$$Weight\,load\ (\%) = \frac{\Delta P}{P_0} \times 00 \qquad (3)$$

where P_0 = the weight of rigid part at time zero; ΔP = the weight difference P - P_0, where P is the weight of the rigid part at the selected times.

4.1.8 Tribological analysis

Friction behavior were studied using a Nanoevea pin-on-disk tribometer from Micro Photonics. The tester consists of a stationary "pin" under an applied load in contact with a rotating disc. The pins used were steel balls (SS302) made by Salem Specialty Ball with 0.32 mm diameter. The normal force applied was 5.0 N.

The schematic diagram of the main apparatus of the friction and wear tester is shown in figure 7. Tribological tests were performed on flexible sPVC-based samples and rigid PVC samples after migration tests. The tests lasted 30 minutes at the sliding velocity of 3000 revolution numbers per minute; the radius of the frictional track on the disk was 2.0 mm.

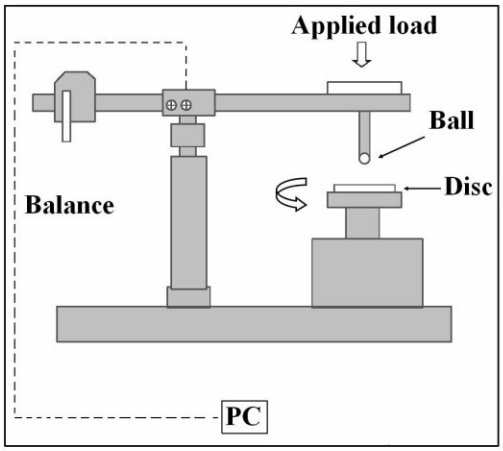


Figure 7. Diagram of pin-on-disk friction and wear test apparatus.

Preliminary experiments at different sliding rates (not reported) were performed in order to find the test conditions able to reduce the points scattering in the friction trace.

4.1.9 Microhardness Measurements

Vickers micro-indentation tests were performed using a dynamic HMV-M Shimadzu Micro Hardness Tester, model M3, from Shimadzu, Kyoto, Japan.

The indentation hardness H_i of a material is expressed as the ratio of the load applied to the area of indentation. Five indentations in randomly selected areas under 100 g load and a 5s holding time were carried out on rigid PVC after being in contact, for 30 days, with flexible sPVC-based samples. The resulting deformation was measured immediately after load release in order to avoid complications associated with viscoelastic recovery. The diagonal length impression were measured and the Vickers hardness was calculated according to equation 4 [5]:

$$h_v = 854.4\frac{P}{d^2} \quad (4)$$

where h_v= Vickers microhardness in kg/mm^2; P = applied load in g; d = mean diagonal length of the indentation mark in μm.

4.2. Results and discussion

4.2. 1 Solvent extraction

As a consequence of the chemical cross-linking reaction promoted by IPDA, a certain amount of gelled portion formed. The results obtained from solvent extraction procedure are reported in table 5.

In the case of pPVC sample, although no cross-linking agent was used in the formulation, a residual gel amount ≈ 13 wt. % was found.

	Samples			
	pPVC	**C1**	**C2**	**C3**
wt % gel	13	24	28	48

Table 5. Weight percentage of gel in flexible PVC samples.

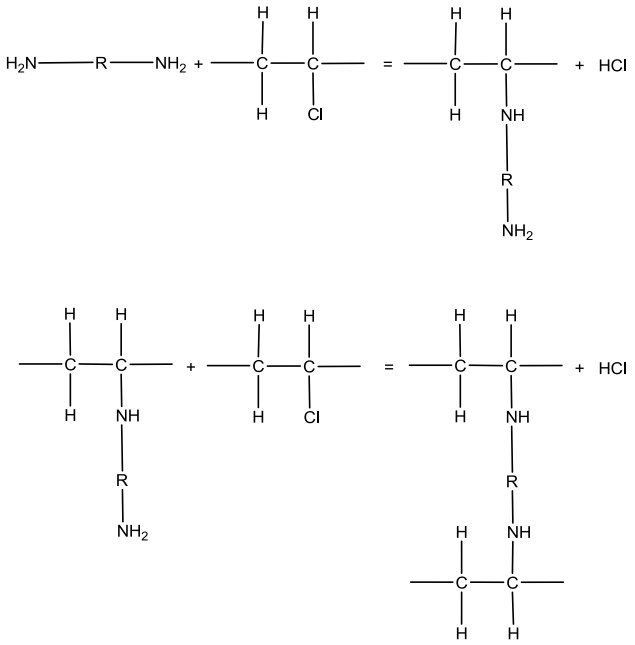
This finding is probably due to cross-linking of polyene sequences formed upon dehydrochlorination (DHCl) caused by fairly high processing temperatures [6, 7].

As already mentioned, there are radical or ionic mechanisms suggested, and the type of reaction depends also on the conditions (temperature, presence of oxygen, etc.) during the decomposition.

In general, in the first stage the DHCl leads to formation of double bonds followed by a so-called rapid zipper-like splitting off of HCl molecules to give polyene sequences [8-11] see scheme 1.

Once they are formed, the polyene sequences can react leading to the cross-linked PVC structure. As we can observe from table 5, in the case of C1, C2, C3 the gel content is higher than that of pPVC. The effect of IPDA on the gel quantity formation can be described in terms of two distinct simultaneous phenomena. Namely, during amine cross-linking the chlorine atom is extracted from the main polymer chain and replaced by a cross-linker unit leading to the formation of N-C bonds [1] (see scheme 2).

The cross-linking reaction involves the loss of two HCl molecules which are responsible for the enhanced catalytic effect on PVC dehydrochlorination and consequently further cross-linking.



Scheme 2. Cross-linking mechanism promoted by IPDA.

4.2.2 Thermogravimetric analysis(TGA)

Thermal stability of flexible sPVC-based samples was evaluated by TGA.

TGA and differential TGA (DTG) diagrams are shown in figure 8.

In table 6 are listed T_{max} = the temperature (define as the maximum of the derivative of the curves) at which the first degradation step occurs; and the weight percentage of char (char %) at 600°C.

The thermal degradation process proceeds in two basic stages. Within the range of 200–400 °C mainly loss of DOP and dehydrochlorination of PVC take place [12]. These two distinct phenomena are clearly observed in the case of pPVC for which the loss of DOP and the DHC1 take place at T = 266°C and T = 289 °C, respectively.

As for samples C1, C2 and C3, they exhibit one broad degradation peak, centred at lower temperatures, indicating simultaneous occurrence of the two phenomena. As stated in section 4.2.1, it is likely that the increased concentration of HC1 due to the use of IPDA is responsible for faster degradation of PVC [13, 14]. As a consequence the DHC1 is shifted at lower temperatures.

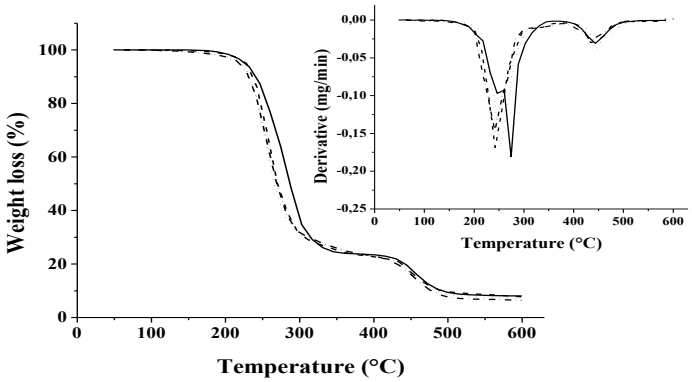


Figure 8. TG and DTG diagrams for pPVC (—), C1 (– – –), C2 (•••), C3 (– • –).

The second degradative stage at T > 400 °C corresponds to scission of covalent bonds in PVC chains. In this step all the samples exhibit the same behavior.

1st degradation step		
Sample	**T_{max} (°C)**	**Char % at 600 °C**
pPVC	289	8.7
C1	257	7.8
C2	254	7.0
C3	254	6.5

Table 6. TGA results in N_2.

4.2.3 Mechanical and dynamic-mechanical properties

The dynamic-mechanical analysis was performed to determine the glass transition temperature (T_g) of all the flexible sPVC-based samples.

The tanδ curves are shown in figure 9 and the corresponding T_g values (at the maximum of tanδ curves) are reported in table 7.

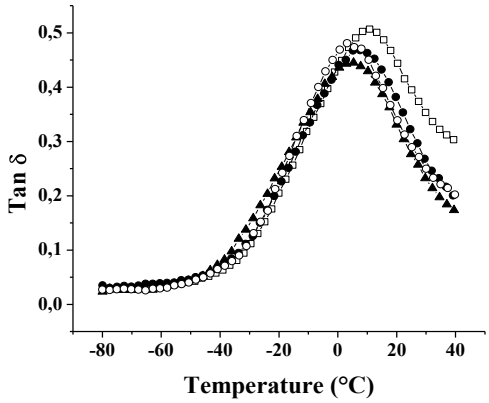


Figure 9. Tanδ curves of pPVC (-□-), C1 (-●-), C2 (-▲-) and C3 (-○-).

Samples C1, C2 and C3 showed lower glass transition temperatures compared to pPVC. This is unexpected, since all the samples contain the same amount of plasticizer, and the cross-linking is likely to lead to a matrix rigidification. Probably, this behavior can be ascribed to the decreasing of molecular weight of PVC macromolecules upon thermal degradation.

Sample	Tg (°C)	E (MPa)	ε_b (%)	σ_b (MPa)
pPVC	11	6.73 ± 0.5	289.78 ± 11.12	9.38 ± 1.8
C1	5.5	6.01 ± 0.4	304.89 ± 14.02	10.38 ± 1.3
C2	3.5	6.05 ± 0.3	319.88 ± 11.47	11.38 ± 2
C3	3.1	4.89 ± 0.4	311.25 ± 11.18	9.38 ± 1.06

Table 7. Mechanical and dynamic-mechanical results.

The tensile properties of uncross-linked and cross-linked flexible PVC samples were measured on mini tensile bars. Typical stress-strain curves are shown in figure 10.

In table 7 are reported the data obtained for E, σ_b and ε_b of the tested samples.

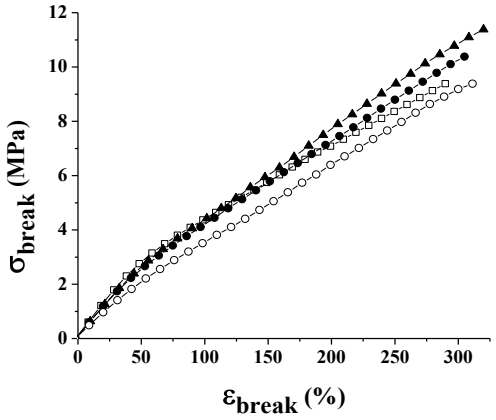


Figure 10. Stress-strain curves of pPVC (-□-), C1 (-●-), C2 (-▲-) and C3 (-○-).

In figure 10 it can be observed that the tensile behavior of the cross-linked samples is similar to that of pPVC. There is no significant difference in the tensile mechanical behavior of the four samples. These results are reasonable since the flexible PVC properties are not sensitive to such a small amount of cross-linker. This is encouraging because the main focus was to reduce the plasticizer migration without affecting the mechanical behavior of the material.

4.2.4 Migration tests

In order to evaluate the effect of cross-linking on the plasticizer migration extent, weight increase of rigid PVC in contact with soft sPVC-based samples were monitored according to equation (3). Figure 11 reports percentage weight variations determined for rigid PVC sheets kept in contact with plasticized samples.

As expected, rigid PVC samples were able to absorb the plasticizer from soft PVC specimens [15]. Higher weight values were found for prolonged contact times. After 30 days the weight increase of rigid PVC sheets kept in contact with soft cross-linked PVCs was about 18 % lower than that of sheets in contact with pPVC sample. Therefore, the cross-linked materials have comparable abilities to retain the plasticizer. This finding proves that PVC chemical cross-linking could be an attractive tool to overcome the disadvantage related to the plasticizer migration. Nevertheless, the amount of DOP migrating from cross-linked samples turned out to be independent of the cross-linker loading. Almost the same quantity of DOP was released by

C1, C2 and C3. To explain this possibly unexpected result we recall that the cross-linking density is different from the cross-linking extent [16].

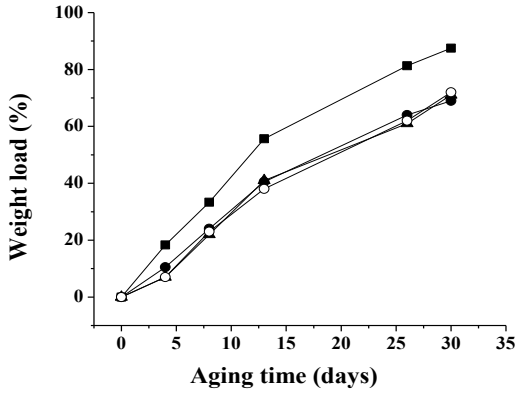


Figure 11. Migration tests. Weight change of rigid PVC sheets after being in contact at 60°C with pPVC (-■-), C1 (-●-), C2 (-▲-), C3 (-○-).

Apparently our samples C1, C2, and C3, even though characterized by different amounts of gel formed (table 5), have comparable cross-linking densities. Further investigation will be carried out in order to determine the cross-linking densities and its effect on migration.

4.2.5 Friction and microhardness

Indirectly, the effectiveness of cross-linking on plasticizer migration was studied by means of tribological analysis. The pin-on-disk technique serves well for the determination of dynamic friction [17, 18]. In figure 12 are shown dynamic friction results for rigid (uPVC) and flexible sPVC-based samples as a function of the number of revolutions.

Rigid PVC is characterized by an average value of dynamic friction ≈ 0.15, which falls in the range between 0.1 and 0.5 typically exhibited by polymers [18]. As expected, the pPVC sample stands apart. The cross-linked samples C1, C2, and C3 exhibit comparable friction values, with C3 (see again table 5) consistently but not by much lower than C1 and C2. We have already inferred that these three samples probably have comparable crosslink density, which brings the three curves together. C3 exhibits the highest extent of gel, thus moving the curve lightly down.

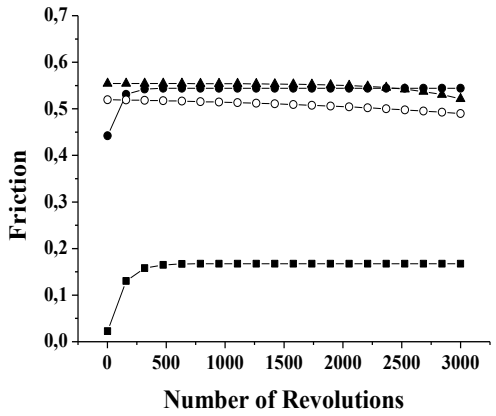


Figure 12. Friction of unaged samples: uPVC (-■-), pPVC (-□-), C1 (-●-), C2 (-▲-), C3 (-○-).

In figure 13 are presented dynamic friction values for rigid PVC sheets contacting for 30 days with flexible sPVC-based systems. Rigid PVC in contact with pPVC exhibits the highest friction values. This is due to the large amount of DOP moved towards the interface, increasing the adhesion between the pin and the sample surface.

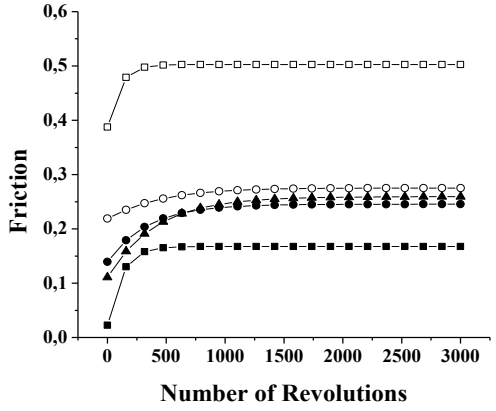


Figure 13. Friction of unaged uPVC (-■-), aged uPVC after being in contact for 30 days with pPVC (-□-), C1 (-●-), C2 (-▲-), C3 (-○-).

Rigid PVC samples in contact with C1, C2 and C3 show comparable friction behavior, relatively close to neat rigid PVC. This finding validated the effectiveness of cross-linking in partially preventing plasticizer migration which is in agreement with plasticizer migration results.

Vickers micro-hardness characterization was also carried out on rigid samples after contacting tests. Micro-hardness is a convenient tool for dealing with surface diffusion of plasticizers consisting essentially of evaluating the dimensions of the impression resulting from the penetration of an indenter under a constant load applied to the surface of a small sample [19, 20]. Micro-hardness values calculated according to equation (4) are listed in table 8. Compared to uPVC, the $h_{Vickers}$ values of the rigid samples held in contact with flexible PVC sheets are by a whole order of magnitude lower. This finding is due to the large surface deformation caused by significant amount of plasticizer absorbed at the interface [21]. Being the surfaces of the rigid PVC samples kept in contact with soft formulations presumably saturated of DOP, after a long-term aging, their deformation is quite similar and thus $h_{Vickers}$ values.

Sample	**Vickers microhardness $h_{Vickers}$**
uPVC	151
uPVC in contact with pPVC	11.5
uPVC in contact with C1	16.1
uPVC in contact with C2	18.3
uPVC in contact with C3	17.7

Table 8. Vickers microhardness values of rigid PVC (uPVC) after being in contact, for 30 days, with sPVC-based samples.

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CHAPTER 5

Substitution of DOP by polymeric plasticizers

In order to reduce the extent of plasticizer migration from the flexible PVC matrix new formulations of flexible polyvinylchloride (PVC) were obtained by replacing low-molecular weight dioctylphtalate (DOP) with poly(butylene adipate)-based plasticizers, with both linear (PBA) and hyper-branched structure (HPBA).
The experimental part was carried out in two stages:

- The synthesis and characterization of hyper-branched poly(butylene adipate), HPBA.
- The preparation and characterization of flexible PVC blends with three different plasticizers: DOP, linear poly(butylene adipate) (Palamoll), and HPBA.

In this work we investigated on the properties of flexible PVC systems plasticized with HPBA. As references for our study two standard formulations of plasticized PVC, one with dioctylphtalate (DOP) and the other with a commercial linear poly(butylene adipate) (Palamoll), were used. The key issue was to obtain a material with an increased migration stability, workable in conventional processing equipments and conditions, matching the technical requirements such as degree of flexibility, thermal and mechanical resistance, and manufactured at a comparable cost of usual flexible PVC.

5.1 Experimental part

5.1.1 Materials for HPBA synthesis

1,4-butanediol (BD) (99%), dimethyl ester of adipic acid (DMA) (99%), the branching agent trimethylol propane (TMP) (98%), the catalyst titanium isopropoxide (TIP) (99.99%), methanol, diethyl ether and chloroform were purchased from Sigma-Aldrich and used without any purification.

5.1.2 Synthesis procedure of HPBA

BD, DMA and TIP were weighted and added to a two neck round-bottom reaction vessel in the amounts reported in table 9. The reaction vessel was immersed in a silicon oil bath and the temperature was increased under nitrogen gas to 150 °C where the reaction was continued under mechanical stirring for 4 h.

Polyester	BD:DMA[b]	TIP (mol%)	TMP (mol%)
HPBA	1.0:1.0	0.2	1.5

Table 9. Reagents amount for HPBA synthesis. [b]Molar Ratio (mole:mole).

The methanol formed, as a consequence of trans-esterification reaction between BD and DMA, was continuously distilled out from the reaction flask. Once obtained the poly(butylene adipate) oligomers, the reaction mixture was cooled down to room temperature and kept at this temperature for 1 hour; then TMP (table 9) was added. The reaction was continued in the same conditions for other 4 hours. The temperature of the reaction mixture was then raised to 180°C under reduced pressure (≈ 10 Torr) and the polymerization was continued for 16 h.
After the polymerization was completed the reaction mixture was cooled down to room temperature. The polyesters was dissolved into chloroform, precipitated into a large excess of methanol, filtrated and washed with diethyl ether. Finally, the white powder was filtrated again and dried under vacuum at 40°C for one day.

5.1.3 Materials for PVC blends

Rigid PVC sheets were prepared using PVC pellets BENVICVIC® IH007W025AA (Solvay Benvic, Italy). The base polymer used for flexible samples (sPVC) was PVC Lacovyl® S7015 PVC (Arkema, France). (Ca + Zn)-based powder Reapak B-NT/7060 (Ca + Zn 0.5-0.8 phr) (Ca/Zn- Reagens, Italy) and epoxy soybean oil (ESBO- Shangai Yanan Oil and Grease Co.) were selected as heat stabilizer and co-thermal stabilizer, respectively. Low-molecular weight commercial plasticizer dioctylphtalate (DOP) DIPLAST® 0 (purity > 95%) was received from Lonza S.p.A., Italy.
A linear, viscous polyester Palamoll® 654 (Palamoll) (BASF Corporation, USA) (Mw = 5200 g/mol, density (25 °C) = 1.0761 g/mL) was selected as a commercial polymeric plasticizer for PVC.

5.1.4 Preparation of sPVC-based blends

All the samples were prepared mixing sPVC, Ca/Zn, ESBO and plasticizers in a roll-milled plasticorder at 40 rpm, T = 120°C for 15 min. The formulations of all flexible sPVC-based blends are reported in detail in table 10.

	Components					
Samples	**PVC (phr)**	**ESBO (phr)**	**Ca/Zn (phr)**	**DOP (phr)**	**Palamoll (phr)**	**HPBA (phr)**
pPVC	100	2	1	70	–	–
L50	100	2	1	–	50	–
L60	100	2	1	–	60	–
L70	100	2	1	–	70	–
L80	100	2	1	–	80	–
H50	100	2	1	–	–	50
H60	100	2	1	–	–	60
H70	100	2	1	–	–	70
H80	100	2	1	–	–	80

Table 10. Flexible sPVC-based formulations.

The flexible sheets with a thickness of 1 mm were obtained using a hot press (lab-scale Collin P 200 E) at 150 °C and 200 bar for 7 min.
Rigid PVC sheets with a thickness of 2 mm were prepared by press-molding the polymer pellets at 190 °C and 200 bar for 7 min.

5.2 Characterization

5.2.1 Nuclear magnetic resonance spectroscopy (NMR)

The HPBA structural analysis was studied by means of nuclear magnetic resonance spectroscopy. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance-600 spectrometer operating at 600 MHz using a TCI probe. The one-dimensional ^{1}H spectra were acquired in 16 scans.

5.2.2 Differential scanning calorimeter (DSC)

The melting behavior of the HPBA sample was investigated using a differential scanning calorimeter (DSC), TA Instruments (mod Q2000). A dynamic heating rate of 10 °C/ min was used. The sample was heated up to 100 °C, held there for 5 min, then cooled down to 10 °C and heated again up to 100 °C.
For isothermal crystallization, about 6 mg hyper-branched polyester-containing pans were first heated to 75 °C, which is about 20 °C above the HPBA melting temperature, held there for 5 min, and then quenched at 10 °C/min to three selected temperature Tc (27, 29, 32 °C) held there for 30 min. After completion of crystallization, the HPBA sample was heated directly from Tc to the melt at a rate of 10 °C/min.

5.2.3 Wide angle X-ray diffraction (WAXD)

A wide-angle X-ray diffractometer Philips model PW 3710 equipped with a rotating-anode X-ray generator was used for the evaluation of hyper-branched polyester and PVC/HPBA blends crystallinity. The scanning 2θ angle was from 2° to 60° with a step scanning of 0.04°/s.

5.2.4. Thermogravimetric analysis (TGA)

The thermal stability of the polymeric plasticizers and their blends with PVC was studied by means of thermogravimetric analysis.
TGA was carried out at 10°C/min heating rate from 25°C to 600 °C under nitrogen flow using a Q5000 (TA Instruments) thermo balance.

5.2.5 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis (DMTA) measurements were carried out using a Triton Technology mod. Tritec 2000 testing machine. Tests were performed in single cantilever bending mode, using a constant frequency of 1 Hz and an amplitude of oscillation of 0,01 mm. Samples were heated from -80°C up to different temperatures (40°C, 60°C, 80°C), depending on the sample, at 5°C/min heating rate. The glass transition temperature, T_g, was taken as the peak temperature of tanδ curve.

5.2.6 Mechanical properties

The Young's modulus (E), ultimate tensile strength (σ_b), and elongation at break (ε_b) were determined from a traction test in an universal dynamometer INSTRON *mod.*5564 at room temperature using 1 KN load cell, at a crosshead speed of 10 mm/min. The dog bone shaped mini tensile bars were characterized by a 2 mm thickness, 4 mm width and 28 mm length.
For each sample a batch of five specimens was tested and the average values were reported.

5.2.7 Migration tests

Plasticizer migration was determined by monitoring weight changes of PVC/Palamoll and PVC/HPBA blends according to the procedure described in section 4.1.7. The specimens removed from the oven at different times were immediately weighted. The weight loss of the exudable flexible component was determined by measuring the samples weight according to equation 5 [1]:

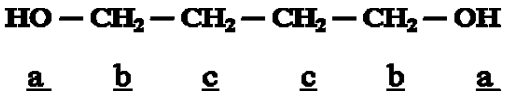
$$\text{Weight loss } (\%) = \frac{W_i - W_t}{W_i \times \frac{70}{173}} \times 100 \qquad (5)$$

where W_i = the initial weight of soft part, W_t = the weight of the soft part at the selected times and the factor 70/173 is related to the amount of the exudable plasticizer.

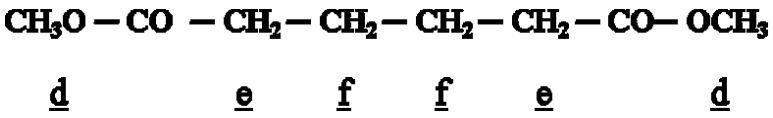
5.3 HPBA characterization: results and discussion

5.3.1 Nuclear Magnetic resonance (NMR) of HPBA

In figure 14 is shown the ^{1}H NMR spectrum of HPBA.
The ^{1}H NMR spectrum of hyper-branched polyester was discussed taking into account the characteristic signals of 1,4 butanediol and dimethyl adipate .
The signals at δ = 4.08 ppm (b) and δ = 1.69 ppm (c) are assigned to 1,4 butanediol, while the signals at δ = 1.65 ppm (f) and δ = 2.32 (e) are assigned to dimethyl adipate as reported below:



1,4 butanediol chemical structure



Dimethyl adipate chimica structure

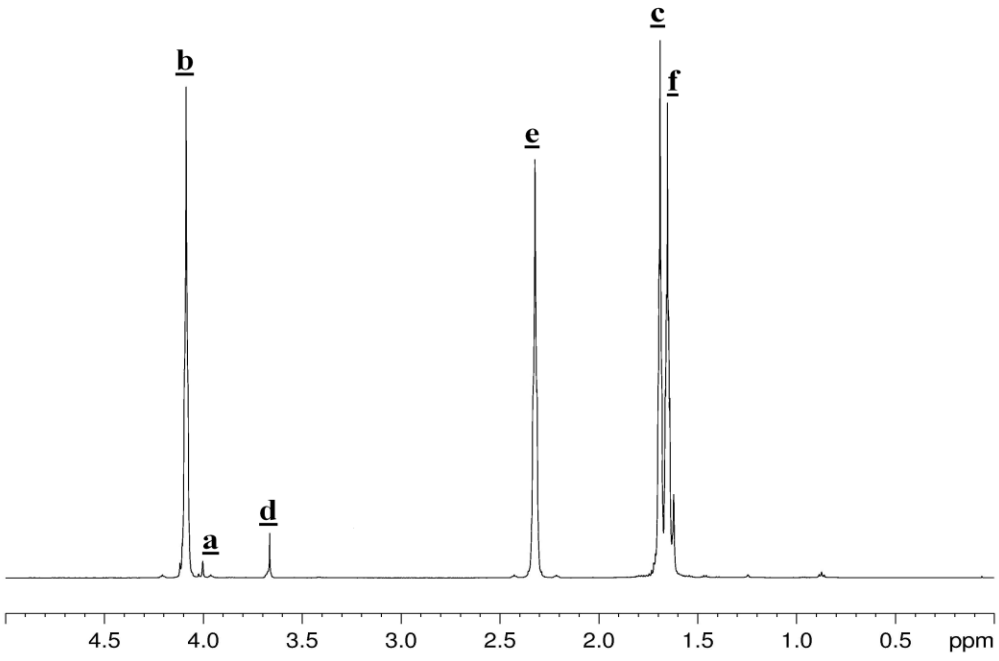
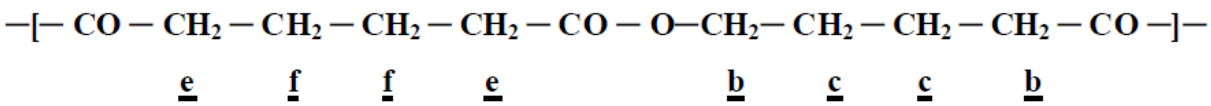


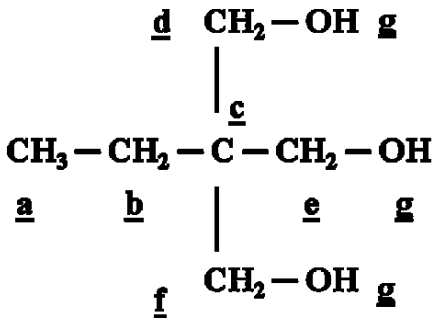
Figure 14. [1]H NMR spectra of HPBA.

As already stated, the trans-esterification reaction between the two monomers leads to the formation of poly(butylene adipate) oligomers:



The intensity ratio between the signals associated to the skeleton groups (-CH_2) and terminal units (a) and (d) (see figure 14) is much higher than that calculated for the reagents, validating the occurrence of the trans-esterification reaction hence the poly(butylene adipate) oligomers formation.

In the second step of the synthesis the cross-linking agent (TMP) was added. Its chemical structure is reported below:



Trimethylol propane (TMP) chemical structure

In figure 15 is shown the ^{1}H NMR spectrum of TMP. The peaks assignment is reported in table 11. The formation of the hyper-branched structure, is revealed by the changes of TMP signals (a), (b) and (g).

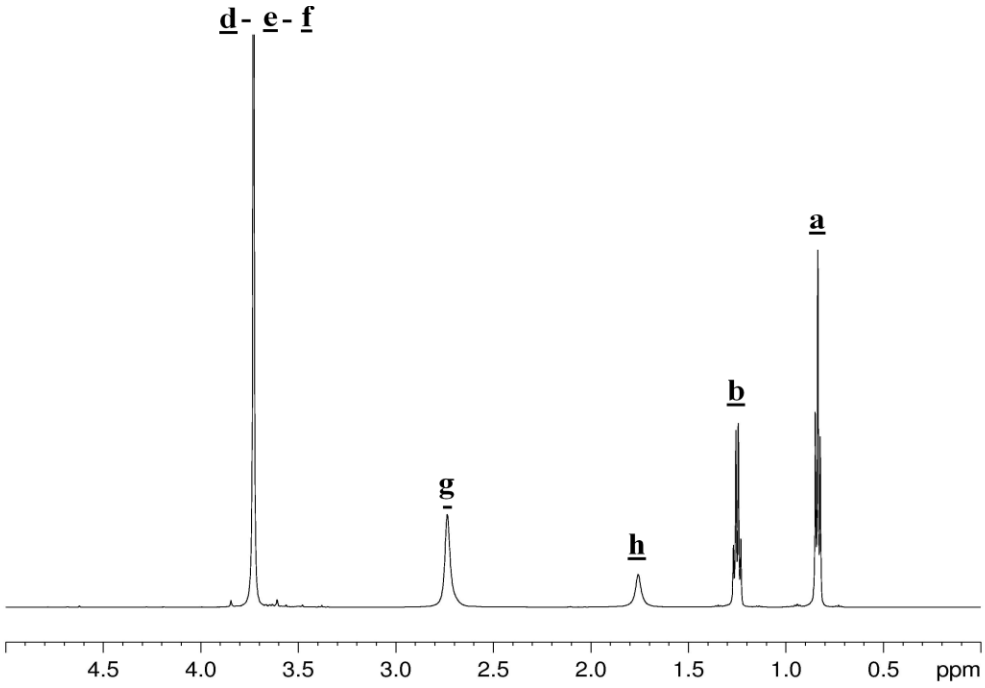


Figure 15. ^{1}H NMR spectra of TMP.

TMP groups	δ (ppm)
a	0.84
b	1.25
d-e-f	3.73
g	2.74
h (H_2O in $CDCl_3$)	1.75

Table 11. TMP peaks assignment.

In figure 16 the TMP and the hyper-branched polyester ^{1}H NMR spectrum are overlapped for comparison. In the HPBA spectrum (see table 12), the TMP signals (a) and (b) are shifted at values (a') and (b') corresponding to (-CH_2) units bounded to the esteric groups formed upon trans-esterification reaction.

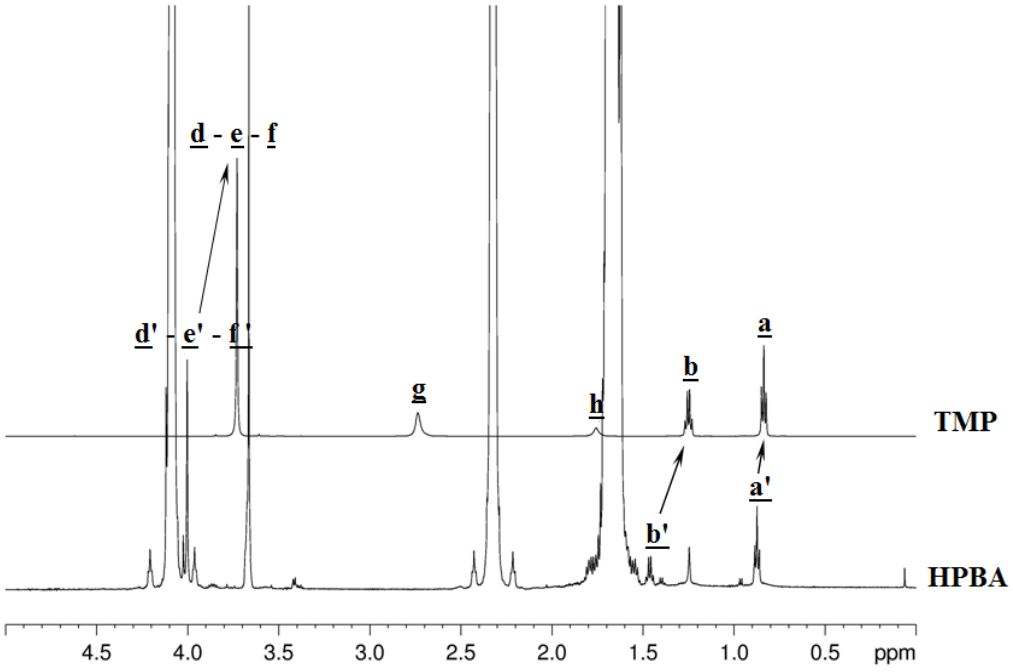


Figure 16. ^{1}HNMR spectrum of HPBA and TMP.

The chemical shifts observed validate the occurrence of the branching reaction.

This finding is further confirmed by the absence of the signal relative to the hydroxyl groups (-OH) of TMP (g) in ^{1}H NMR spectrum of HPBA.

TMP groups	δ (ppm)
a’	0.88
b’	1.46
d’ - e’ - f’	4.00
g’	missing

Table 12. TMP peaks assignment, in the polymer.

5.3.2 Differential scanning calorimetry (DSC)

The melting behavior of the HPBA sample was investigated by differential scanning calorimetry. In figure 17 is reported the DSC curves of HPBA.

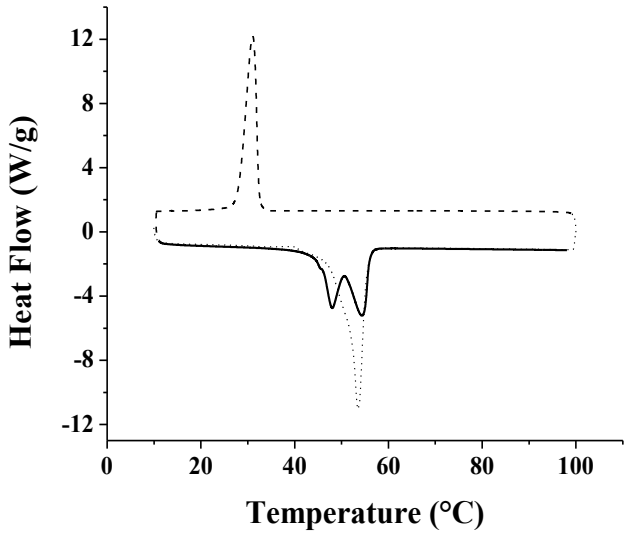


Figure 17. DSC curves of HPBA: first heating scan (…), cooling scan (---) second heating scan (—).

In the first heating scan a wide shape melting peak is observable, whose maximum is associated to a melting temperature of 53 °C. Furthermore, a side shoulder is visible around 50 °C. When the sample was cooled down a single crystallization temperature of 31 °C was found. However, in the second heating scan, two melting peaks at 48 °C and 54 °C were found. As reported in literature, the polymorphism phenomena usually has been observed in poly(butylene adipate), PBA [2, 3]. The poly(butilene adipate) is characterized by a rather complex melting behavior.

Temperature is an important factor in favoring a specific type of crystal formation in polymorphic polymers. A general finding is that the formation of α-and β-form crystals and their relative fractions in poly(butylene adipate) is dependent on the melt crystallization temperatures (figure 18).

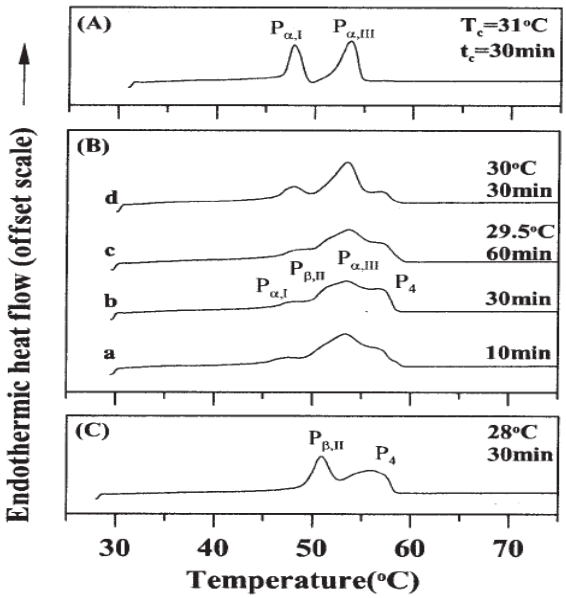


Figure 18. DSC for PBA crystallized at three temperature regimes: (A) high-T, (B) intermediate-T, and (C) low-T.

Doi and coworkers [3] have pointed out that the poly(butylene adipate) chains are packed as the α-form crystal melt-crystallized at temperatures above 31 °C, while the β-crystal is the dominating species crystallized at temperatures below 29 °C. The PBA, which has both crystalline forms can display up to four melting peaks (P1-P4). If the poly(butylene adipate) contains only α-form or β-form, only two melting peaks appear which can be attributed to the double distribution of lamellar α- or β-crystals.

Drawing on the work on PBA, three different temperatures 27, 29 and 32 °C were chosen for the DSC isothermal crystallization run (section 5.2.2) in order to investigate the polymorphism of HPBA.

The DSC curves obtained after melt-crystallized in the temperature ranges from 27 to 32 °C are reported. After isothermal (30 min) crystallization at 27 °C, figure 19 (a), two melting peaks appear at 50 and 56 ° C which could correspond to the β-crystalline form.

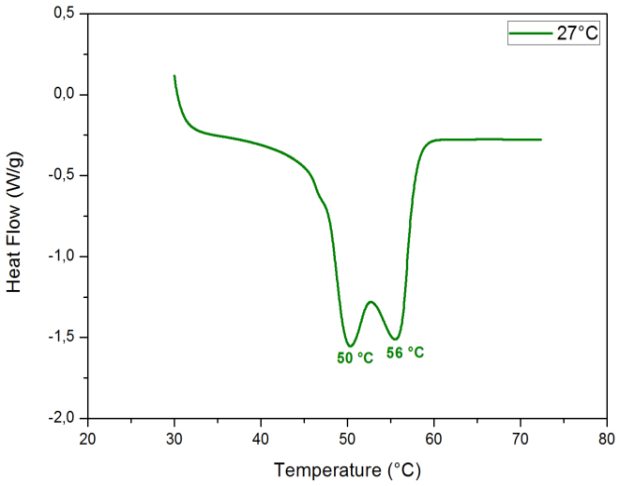


Figure 19 (a). DSC curves for HPBA obtained after melt-crystallized at 27 °C.

After isothermal (30 min) crystallization at 32 °C, figure 19 (b), two melting peaks appear at 48 and 53 ° C which could correspond to the α-crystalline form.

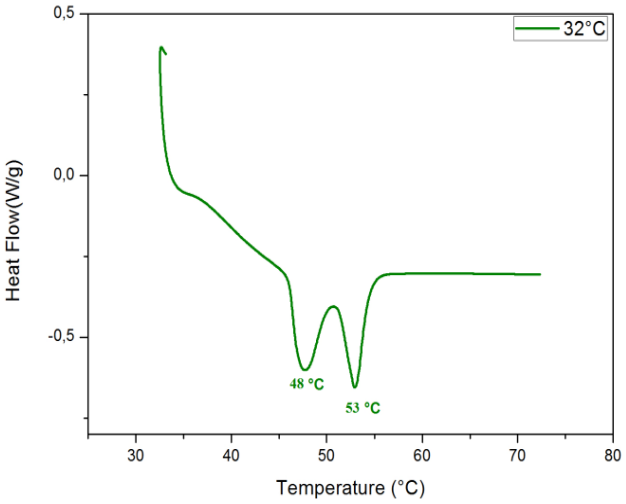


Figure 19 (b). DSC curves for HPBA obtained after melt-crystallized at 32 °C.

In the last isothermal (30 min) crystallization run at 29 °C, figure 19 (c), a wide melting peak is located at 54 °C showing also two shoulders centered at 46 and 51 °C respectively. This result probably is due to the coexistence of both α and β forms.

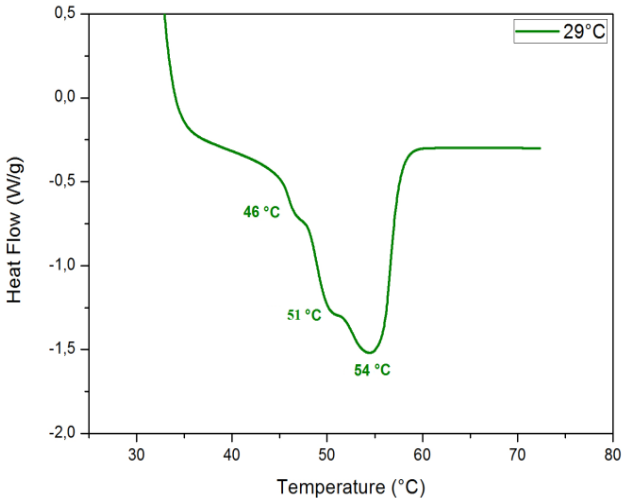


Figure 19 (c). DSC curves for HPBA obtained after melt-crystallized at 29 °C.

It is likely to state that polymorphism phenomena of HPBA could be related to long linear side chains polymorphism behavior of poly(butylene adipate).

5.3.3 Wide angle X-ray diffraction (WAXD)

The HPBA morphology was studied by X-ray technique figure 20 shows the X-ray diffraction pattern of hyper-branched poly(butylene adipate) (HPBA).

Two diffraction peaks located at 21.35 ° and 24.55 ° are observed thus confirming the crystalline structure of the polymer.

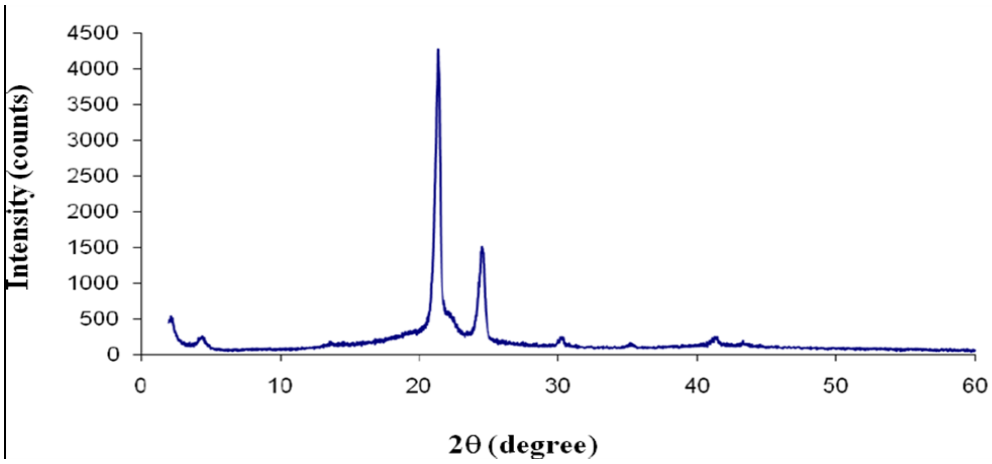


Figure 20. HPBA wide angle X-ray diffractogram.

5.3.4 Thermogravimetric analysis (TGA)

The HPBA thermal stability was studied by means of thermogravimetric analysis.

In figure 21 the TG curves of DOP and Palamoll are overlapped for comparison.

In table 13 is reported $T_{5\%}$ = onset temperature of a 5% weight loss deviation from baseline; T_{max} = the maximum degradation temperature (define as the maximum of the derivative of the curves).

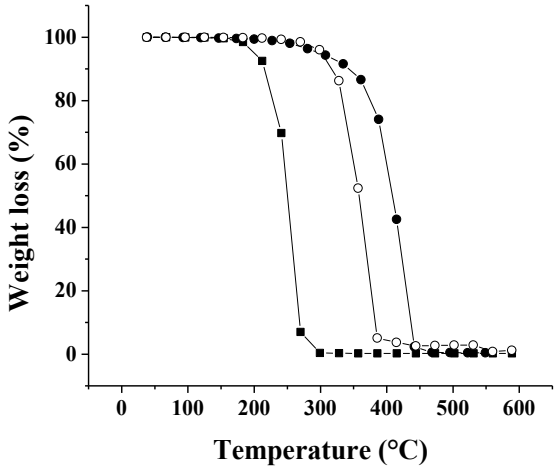


Figure 21. TG curves of DOP (-■-), Palamoll (-●-) and HPBA (-○-).

It can be noticed that HPBA, Palamoll and DOP are thermally stable up to 305, 298 and 204 °C respectively. Above this temperature interval, the plasticizers undergo the thermal degradation. Palamoll is characterized by the highest T_{max} value while faster degradation occur for DOP and HPBA samples.

Sample / TGA results	HPBA	Palamoll	DOP
$T_{5\%}$ (°C)	305	298	204
T_{max} (°C)	369	426	267

Table 13. TGA results for plasticizers.

5.4 PVC blends characterization: results and discussion.

5.4.1 Thermogravimetric analysis (TGA)

sPVC/Palamoll TG curves are reported in figure 22 and sPVC/HBPA TG curves in figure 23, pPVC TG curve is also reported for comparison.

The onset temperature ($T_{5\%}$) and T_{max} values of the first degradation step are reported in table 14.

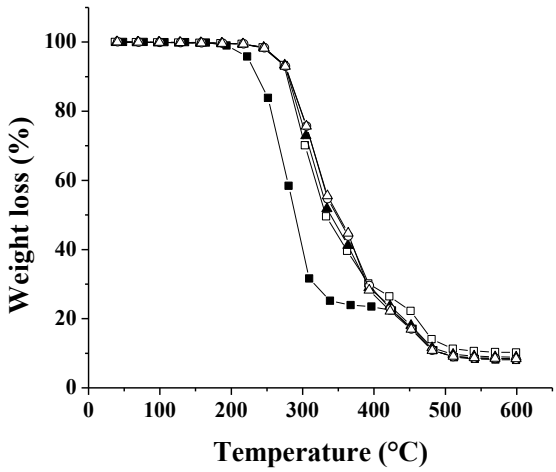


Figure 22. TG curves for pPVC (-■-), L50 (-□-), L60 (-▲-), L70 (-○-), L80 (-◭-).

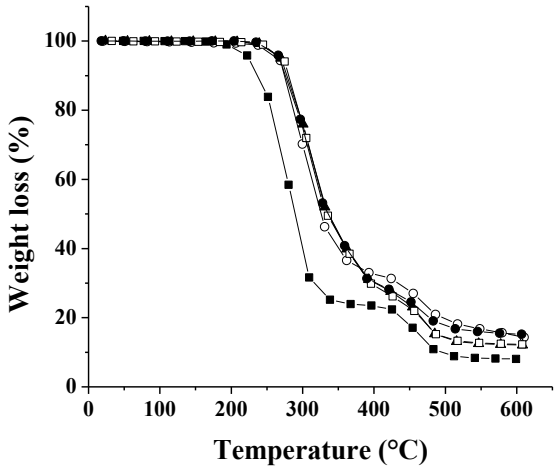


Figure 23. TG curves for pPVC (-■-), H50 (-○-), H60 (-▲-), H70 (-□-), H80 (-●-).

The pPVC thermal behavior has been widely explained in section 4.2.2. Since HPBA and Palamoll are basically more stable at heating, their presence in PVC increased the blends thermal stability. The onset temperature ($T_{5\%}$) was increased by 40 °C when the polymeric plasticizers were employed, regardless of the polyesters amount used. This greater thermal stability was also proved by higher T_{max} values (in the first degradation step) indicating that the PVC dehydrochlorination reaction was slowed down.

Sample / TGA results	pPVC	L50	L60	L70	L80	H50	H60	H70	H80
$T_{5\%}$ (°C)	227	268	269	269	268	265	270	272	268
T_{max} (°C)	289	294	298	308	305	299	298	300	292

Table 14. TGA results for sPVC-based blends.

5.4.2 Wide angle X-ray diffraction (WAXD)

WAXD was used to investigate the morphology of PVC/HPBA blends. We chose to report only the WAXD pattern of H80 (figure 24) since it contains the maximum amount of polymeric plasticizer. Any signal related to the HPBA crystallinity are visible meaning that HPBA looses its structure when added to PVC. The blends are amorphus at any PVC/HPBA ratio indicating good miscibility between the polymers.

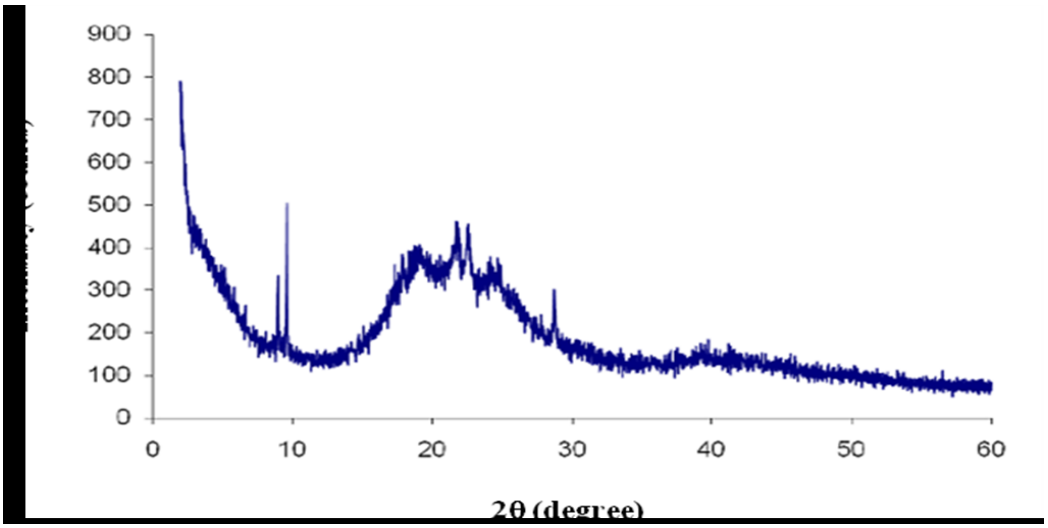


Figure 24. Wide angle X-ray diffractogram for H80.

5.4.3 Mechanical and dynamical mechanical properties

The dynamic-mechanical analysis was performed to determine the glass transition temperature (T_g) of the sPVC-based blends. The trend of T_gs was used as an indirect tool to evaluate the extent of compatibility between PVC and polymeric plasticizers.

In table 15 the T_g values (at the maximum of tanδ curves) of all the samples are reported.

The sPVC/HPBA (figure 25) and sPVC/Palamoll (figure 26) tanδ traces are reported as a function of temperature.

Sample / DMA results	pPVC	L50	L60	L70	L80	H50	H60	H70	H80
T_g (°C)	11	30	18	15	7	39	29	23	18

Table 15. Tg values for sPVC-based blends.

A single glass transition temperature was observed at each composition indicating miscibility between the two polymer components. Monotonic shift of transition temperatures toward low values are observed with increasing the amount of polymeric plasticizers.

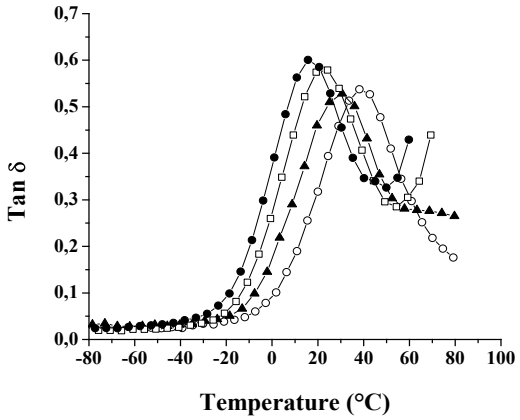


Figure 25. DMTA curves for H50 (-○-), H60 (-▲-), H70 (-□-), H80 (-●-).

This compositional dependence of single T_g indicates that PVC/poly(butylene adipate)s are miscible. The high miscibility between polyester and PVC is due to the hydrogen bonding between the carbonyl group of the ester and the α-hydrogen next to the chlorine atom in PVC.

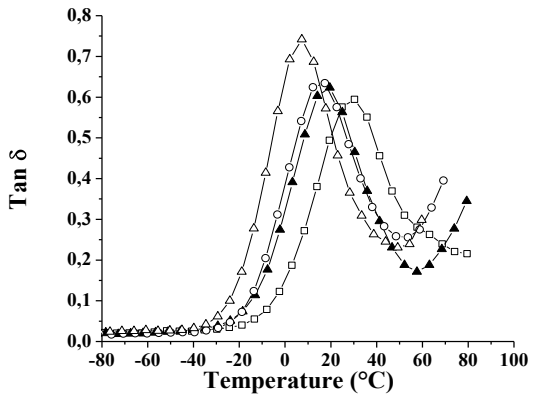


Figure 26. DMTA curves for L50 (-□-), L60 (-▲-), L70 (-○-), L80 (-🜂-).

Comparing the samples containing the same amount of plasticizer, each PVC-HPBA based system showed a T_g value of about ten degrees higher than the corresponding PVC-Palamoll based blend and pPVC. This is probably due to the higher molecular weight of HPBA which restricts the macromolecules mobility. A low molecular weight plasticizer is easily mixed with the polymer resin and its high chain ends density induces much free volume in the material.

The tensile properties of flexible PVC blends were measured on mini tensile bars.

The Young's modulus (E), ultimate tensile strength (σ_b) and elongation at break (ε_b) of sPVC/Palamoll (table 16) and sPVC/HPBA (table 17) blends are reported and compared with flexible PVC plasticized with DOP (pPVC).

Tensile results	Sample				
	pPVC	**L50**	**L60**	**L70**	**L80**
E (MPa)	6.73 ± 0.5	10.43 ± 0.78	7.82 ± 0.55	6.48 ± 0.55	4.56 ± 0.53
ε_b (%)	287.78 ± 11.12	289.84 ± 21.98	296.53 ± 48.77	343.02 ± 24.49	353.65 ± 33.01
σ_b (MPa)	9.38 ± 1.8	17.10 ± 0.73	12.58 ± 1.99	12.49 ± 0.92	8.94 ± 0.76

Table 16. Mechanical properties of sPVC/Palamoll blends.

Plasticizer contents is the most important parameter for the evaluation of plasticizing effects on PVC systems. Monotonic shift of the tensile modulus toward low values was observed with

increasing the amount of both polymeric plasticizers. This finding attests the good plasticizing efficiency of the polyesters which can be used as alternative plasticizers in sPVC formulations.

Tensile results	Sample				
	pPVC	**H50**	**H60**	**H70**	**H80**
E (MPa)	6.73 ± 0.5	10.43 ± 0.78	7.82 ± 0.55	6.48 ± 0.55	4.56 ± 0.53
ε_b (%)	287.78 ± 11.12	314.24 ± 5.12	316.30 ± 16.10	314.36 ± 8.83	378.22 ± 16.83
σ_b (MPa)	9.38 ± 1.8	19.47 ± 0.44	18.44 ± 0.52	14.31 ± 0.42	13.33 ± 0.78

Table 17. Mechanical properties of sPVC/HPBA blends.

In figure 27 the stress-strain curves are shown for pPVC, L70, H70.

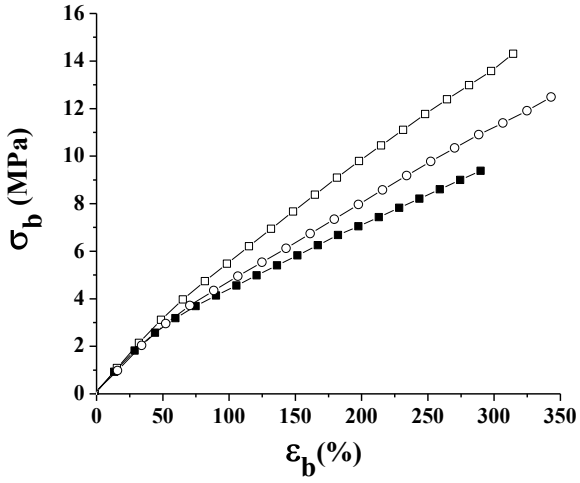


Figure 27. Stress-strain curves for pPVC (-■-), L70 (-○-), H70 (-□-).

Higher stress values were observed for blends containing polymeric plasticizers indicating the superior interphase adhesion and the interfacial tension between the PVC and polybuthylene adipate phase.

5.4.4 Migration tests

Since the polymeric plasticizers were expected to have better migration stability compared to the monomeric one (DOP), migration tests were performed according to section 4.1.7.

The weight loss of the exudable flexible component was determined by measuring the weights of the samples according to equation (5), at different aging times, i.e t =1, 4, 8, 15, 25 and 30 days. Figure 28 shows the curves of weight loss percent vs aging time of pPVC, L70 and H70. A reduced migration of polymeric plasticizers compared to DOP is evident. There are three relevant plasticizer molecular properties that control plasticizer retention: molecular weight, polarity and linearity.

Plasticizer mobility is one of the main factors governing plasticizer the diffusion out of the polymer structure. It is common to relate plasticizer mobility with plasticizer molecular weight. The smaller the plasticizer molecular weight, the greater plasticizer volatility and diffusivity. The superior migration stability of the PVC/polymeric plasticizers is anticipated to their much higher molecular weights in comparison with monomeric DOP [4-6].

Wilson also showed that the migration can be potentially reduced increasing the plasticizer molecular weight and decreasing the linearity of plasticizer. As a matter of fact, HPBA-based blends exhibit a reduced exudation compared to PBA and DOP (see figure 28).

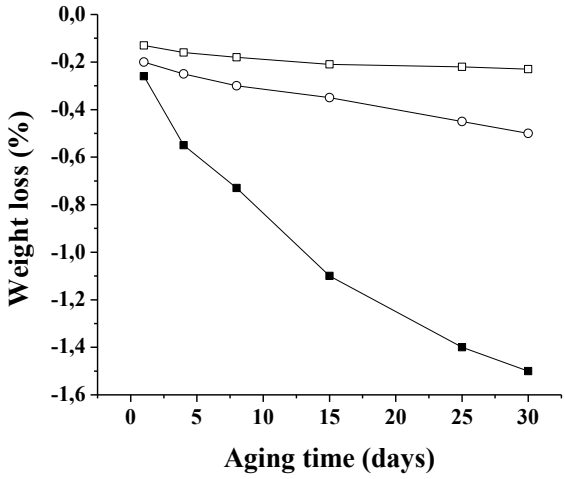


Figure 28. Migration test. Weight loss (%) of pPVC (-■-), L70 (-○-), H70 (-□-).

The polymer's high molar mass and bulkiness significantly reduces its volatility and diffusivity compared to low molar mass plasticizers [1]. Moreover, the high miscibility between polyester and PVC could be responsible for the reduced migration tendency [6]. Since hyper-branched polymers have a higher density of functionality compared to linear polymers of the same molar

mass, they can give rise to effective molecular interactions with PVC leading to higher migration stability systems. As expected, HPBA containing system exhibited the lowest values of weight loss, which remain constant with the aging time, meaning that an efficient plasticizer retention was achieved by the use of highly branched poly(butylene adipate).

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CHAPTER 6

Chlorinated polyethylene (CPE) as a physic barrier to DOP migration

6.1 Chlorinated Polyethylene (CPE, CM)

CPE is the standardized acronym for thermoplastic chlorinated polyethylene. In ASTM D1418 the CPE is designated as "CM", where "C" stands for "chlorine" and "M" denotes "a type of saturated polymethylene chain". The CPE and CM terms are both used in the industrial sector, but in this thesis we will refer only to the first.

Chlorinated polyethylene (CPE) (figure 29), is produced from LDPE (low density polyethylene) and HDPE (High Density Polyethylene).

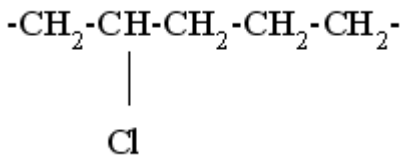

Figure 29. CPE chemical structure.

Chlorine content could be as high as 70% by weight but usually the CPE on the market has a chlorine content in the range 25-42 wt %. The polyethylene molecular weight, from which we obtain the CPE, plays a major role in determining the viscosity of the CPE product.

Higher PE molecular weights give to CPE resin high Mooney viscosity values. In addition, also the CPE chlorine content influences the viscosity. Starting from the same PE, the CPE viscosity increases with increasing the chlorine percentage. Chlorinated polyethylenes (CPE) represent an important class of commercial polymers [1]. CPE is rarely used alone, it is basically employed in blends with other plastics.

The CPE based compounds properties are influenced by the chlorine percentage (see figure 30). The addition of chlorine atom to the PE backbone provides polarity to the polymer structure increasing its chemical resistance and consequently the chemical resistant of CPE based compounds [2].

Depending on the methods used in its production (chlorination in suspension, solution and solid-state), the CPE is characterized by specific performance when mixed with other polymers. Usually, when the chlorination is carried out in solution, chlorine atoms are randomly distributed along the PE macromolecules. However, by suspension and solid-state chlorination, the distribution may be either random (when the process is carried out at temperatures close the PE

melting point) or "block-like" (when the chlorination is performed at temperatures below 100 °C) [3]. A change in the properties is achieved by changing, not only the content of chlorine in polyethylene (PE), but also the ratio between the blend components.

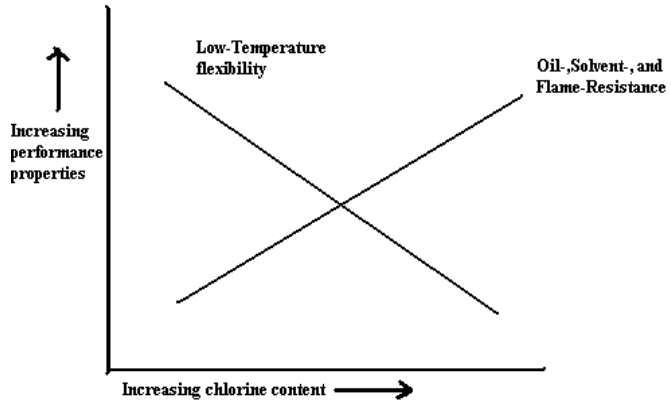

Figure 30. Effect of chlorine content on compounds properties.

The dependence of PVC/CPE softening temperature on the degree of PE chlorination and the CPE amount (wt %) in the blend is shown in figure 31. The blends softening temperature decreases at CPE chlorine content of 22-25 wt %, higher the percentage of chlorine lower is the blend softening temperature. This behavior is probably related to the effect exerted by non-chlorinated methylene groups in CPE, resulting in weakening of the polar interactions between the two polymers. At higher chlorine content in CPE (above 25%), the blends softening temperatures increase due to the stronger polar interactions between the chlorine containing groups of the two polymers [4].

CPE has been recommended as an additive to un-plasticized PVC (uPVC) for several reasons [5] CPEs are highly compatible with PVC because of the different distribution of chlorine (Cl) atoms along the polyethylene chains [6, 7].

The addition of CPE into uPVC raises its impact strength and fire resistance, reduces brittle point, and improves the electrical and other properties [8]. Of particular importance is the use of CPE as a high molecular weight plasticizer to improve the PVC physic-mechanical properties. On the contrary to low-molecular weight plasticizers, CPE is nonvolatile and does not migrate in blends with PVC; therefore, the plasticized compositions have a considerably higher service life.

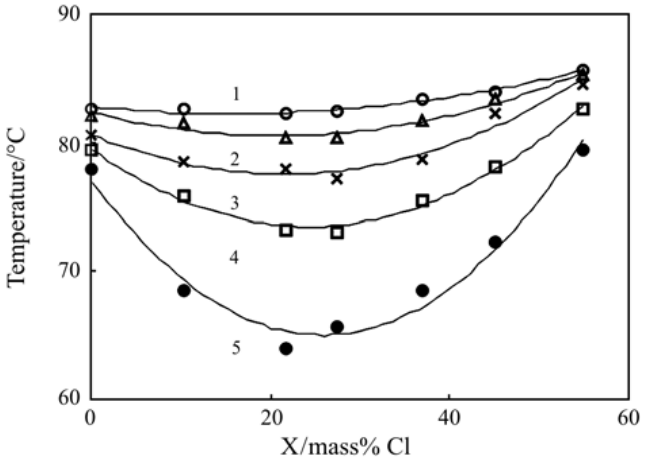

Figure 31. Dependence of PVC/CPE softening temperature on the degree of chlorination at 1-10, 2-20, 3-30, 4-50 and 5-75 % by weight of CPE.

To the best of our knowledge CPE has never been compounded with flexible PVC.
In this work, CPE was used, in flexible formulation, as a physical tool to create a barrier against DOP migration. This approach was considered after preliminary studies on DOP-CPE solubility. DOP was used as "solvent" of a certain amount of CPE forming a slurry viscous fluid. When uPVC was added into DOP, the formation of a gelled system was observed. This result suggested a preferential affinity of DOP to CPE that was expected to improve the CPE ability to retain the plasticizer.

6.2 Experimental part

6.2.1 Materials

The base polymer used for flexible samples was PVC Lacovyl® S7015 PVC (sPVC - Arkema, France). (Ca + Zn)-based powder Reapak B-NT/7060 (Ca + Zn 0.5-0.8 phr) (Ca/Zn- Reagens, Italy) and epoxy soybean oil (ESBO- Shangai Yanan Oil and Grease Co.) were selected as heat stabilizer and co-thermal stabilizer, respectively. Low-molecular weight commercial plasticizer dioctylphtalate (DOP) DIPLAST® 0 (purity > 95%) was received from Lonza S.p.A., Italy. Three different type of CPE pellets were supplied by Faraplan S.p.A. The main characteristics of the three CPEs used are shown in table 18. The rigid PVC sheets used for migration tests were prepared by PVC pellets BENVICVIC® IH007W025AA (Solvay Benvic, Italy).

CPE type	Chlorine content (wt.%)	Mooney viscosity
CPE252	24-26	50-56
CPE6135A	35-37	95-105
CPE3680	35-37	80-90

Table 18. CPE Types used in flexible PVC blends.

6.2.2 Sample preparation

CPE matrices were melt blended with flexible PVC (pPVC). Formulations containing 7 wt.% and 15 wt.% of each CPE were prepared (formulations are listed in table 19) using a plasticorder (mod. PLE 67152 Brabender) at 16 rpm, T = 120 °C for 7 min. The flexible sheets were obtained by press molding (lab-scale Collin P 200 E) the PVC/CPE blends at 150 °C, 200 bar for 7 min. Rigid PVC sheets were prepared by press-molding the polymer pellets at 190 °C, 200 bar for 7 min.

Component / Sample	sPVC	DOP	ESBO	Ca/Zn	CPE
pPVC	100 phr	70 phr	2 phr	1 phr	-
*pPVC/CPE(7%)	100 phr	70 phr	2 phr	1 phr	7 wt.%
*pPVC/CPE(15%)	100 phr	70 phr	2 phr	1 phr	15 wt.%

Table 19. pPVC/CPEs formulations. *The formulation was prepared using the three different CPEs.

6.2.3 Thermogravimetric analysis (TGA)

The thermal stability of flexible pPVC/CPEs blends was evaluated by TGA. Thermogravimetric analysis (TGA) was carried out at 10°C/min heating rate from 25°C to 600 °C under nitrogen flow using a Q5000 (TA Instruments) thermo balance.

6.2.4 Dynamic Mechanical Thermal Analysis (DMTA)

A Tritec2000 DMA by Triton Technology in single cantilever bending mode was used to measure the glass transition temperature of pPVC/CPE blends. Rectangular samples of 1 cm wide, about 2 mm thick and length of approximately 10 mm were used. Tests were performed using a constant frequency of 1 Hz and 0,01 mm oscillation amplitude. Samples were heated from -80°C to 40/80 °C depending on the samples at 5°C/min heating rate. The glass transition temperature (T_g) was taken as the peak temperature of tanδ curve.

6.2.5 Mechanical Properties

Tensile tests were carried out on flexible pPVC/CPEs blends. The Young's modulus (E), the ultimate tensile strength (σ_b) and elongation at break (ε_b) were determined from a traction test in an universal dynamometer INSTRON *mod.*5564.
Samples of about 2 mm thickness, 4mm wide and length of 28 mm were tested at room temperature using a 1 KN load cell with an extension rate of 10 mm/min. A batch of five specimens was used for each sample and the average values were reported.

6.2.6 Migration tests

Plasticizer migration was determined by monitoring weight changes of pPVC/CPE blends according to the procedure described in section 4.1.7. The specimens removed from the oven at different times were immediately weighted. The weight loss of the exudable flexible component was determined by measuring the weights of the samples according to equation (5).

6.2.7 Tribological analysis

Tribological properties were studied using a Nanoevea pin-on-disk tribometer from Micro Photonics. The pins used were steel balls (SS302) made by Salem Specialty Ball with 0.32 mm diameter. The normal force applied was 5.0 N. Tribological tests were performed on pPVC/CPE blends. The tests lasted 30 minutes at the sliding velocity of 3000 revolution numbers per minute; the radius of the frictional track on the disk was 2.0 mm. Preliminary experiments at different sliding rates (not reported) were performed in order to find the test conditions able to reduce the points scattering in the friction trace.

6.3 Results and discussion

6.3.1 Thermogravimetric analysis (TGA)

The thermal stability of CPE and its blends with PVC was studied by means of thermogravimetric analysis (TGA).

Since all the three CPEs used showed the same degradation behavior only the thermograms of CPE6135A and its blend with flexible PVC (pPVC) were reported. For comparison in figure 32 are shown the TG and DTG (inset) degradation curves of the PVC resin (sPVC) and CPE6135A.

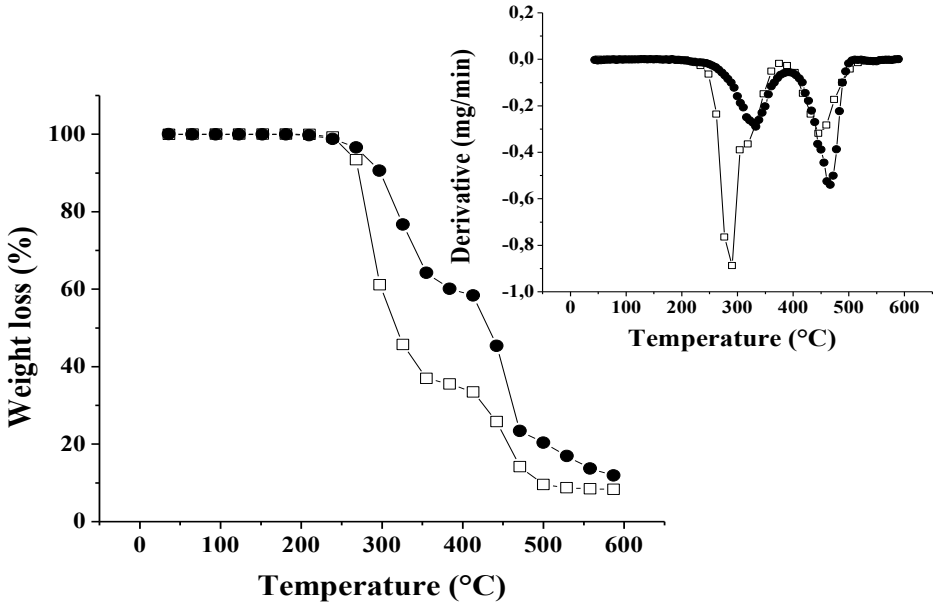

Figure 32. TG and DTG (inset) degradation curves for sPVC (-□-) and CPE6135A (-●-).

The thermal degradation of PVC proceeds in two distinct stages [9-11]. The first stage (200-400 °C) corresponded to the dehydrochlorination of the PVC with the simultaneous formation of conjugated double bonds in the polymer backbone after the splitting off the HC1 molecules (initiation reaction). This was considered to be the main reaction, and HC1 was assumed to be the major volatile product of degradation. The second stage (400-600 °C) corresponded to the scission of polyene structure sequences formed upon the first degradation stage [12, 13].

Similar to PVC, dehydrochlorination was also the dominant reaction in CPE thermal degradation. While the DHCl of PVC is an autocatalytic reaction, the CPE dehydrochlorination is statistical [14, 15].

CPE6135A and sPVC TGA results are reported in table 20 namely: $T_{5\%}$ = onset temperature of a 5% weight loss deviation from baseline; T_1 = the maximum temperature at which the first degradation step occurs; and T_2 = the maximum temperature at which the second degradation step occurs.

TGA results / Neat component	$T_{5\%}$ (°C)	T_1 (°C)	T_2 (°C)
sPVC	265	284	448
CPE6135A	286	330	465

Table 20. Thermogravimetric analysis results.

In contrast to sPVC, the CPE onset temperature ($T_{5\%}$) was increased by 20 °C indicating its better thermal stability. Both CPE degradation stages were located at slightly higher temperature with T_1 at 330°C and T_2 at 465 °C. T_1 value, related to dehydrochlorination reaction, is also a proof of CPE better thermal stability compared to polyvinylchloride .

Klaric et al. [16] reported that the saturated backbone and partly crystalline structure of CPE were responsible for the good thermal stability of CPE before HCl started to evolve.

In table 21 are reported $T_{5\%}$ = onset temperature of a 5% weight loss deviation from baseline; T_1 = the maximum temperature at which DHCl occurs.

Figure 33 shows the TG and DTG (inset) degradation curves of pPVC and its blends with CPE6135A.

Sample	1st degradation step	
	$T_{5\%}$ (°C)	T_1 (°C)
pPVC	227	289
pPVC/CPE6135A (7%)	227	297
pPVC/CPE6135A (15%)	229	298

Table 21. Thermogravimetric results for pPVC and its blends with CPE6135A.

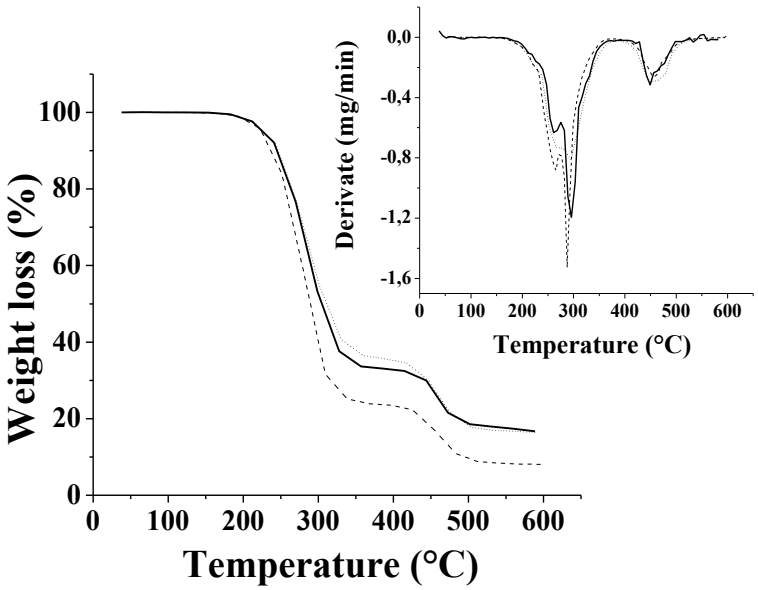

Figure 33. TG and DTG (inset) degradation curves of pPVC (---), pPVC/CPE6135A(7%) (—), pPVC/CPE6135A(15%) (…).

The pPVC thermal degradation process proceeds in two basic stages.

As already stated in section 4.2.2 within the range 200-400 °C, loss of DOP at 266 °C and PVC dehydrochlorination at 289 °C (T_1) take place [17].

When CPE was added to pPVC these two peaks are still visible with T_1 shifted at slightly higher temperatures. The flexible PVC thermal stability was improved to some extent by the addition of CPE regardless of its concentration since CPEs are thermally more stable than PVC.

The degradation step occurring at temperature > 400 °C is not influenced by the addition of CPE.

6.3.2 Mechanical and dynamic-mechanical analysis

The pPVC/CPEs blends were analyzed by dynamic-mechanical analysis (DMA).

The graphs of tanδ as a function of temperature for all the samples characterized are reported.

The Tanδ curves of pPVC/CPE252 containing 7 and 15 wt % of CPE are reported in figure 34 and compared with pPVC.

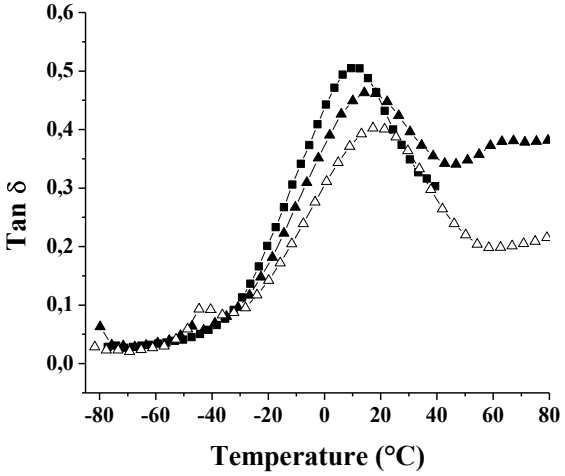

Figure 34. Tanδ curves of pPVC (-■-), pPVC/CPE252(7%) (-▲-),pPVC/CPE252(15%) (-△-).

The curves of pPVC and its blends with different amount of CPE6135A and CPE3680 are shown in figure 35 and 36, respectively.

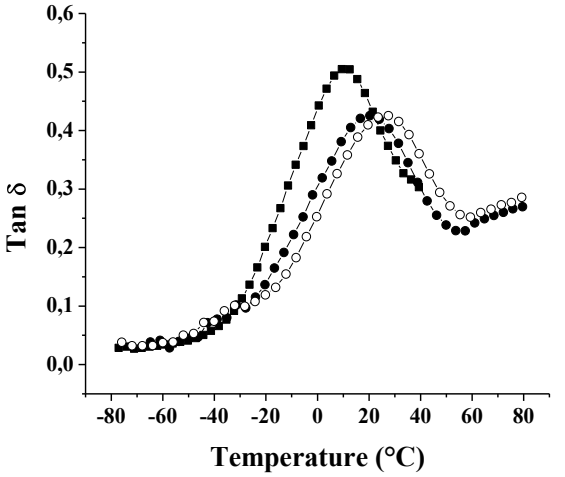

Figure 35. Tanδ curves of pPVC (-■-), pPVC/CPE6135A(7%) (-●-),pPVC/CPE6135A(15%) (-○-).

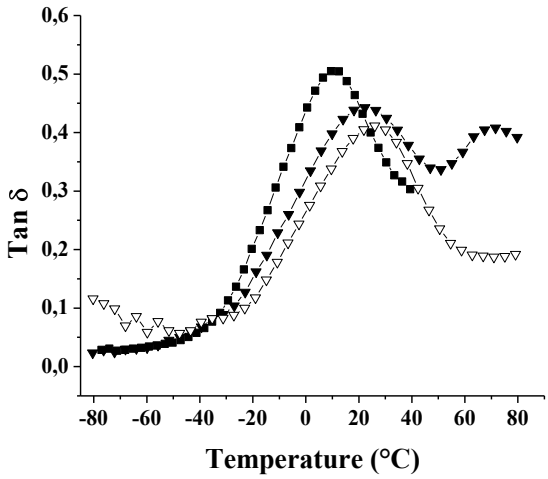

Figure 36. Tanδ curves of pPVC (-■-), pPVC/CPE3680(7%) (-▼-),pPVC/CPE3680(15%) (-◪-).

The Tg values obtained from DMA analysis are reported in table 22.

A single glass transition temperature was observed at each composition indicating miscibility between the two polymers.

The CPEs have a stiffening effect on flexible PVC. The higher the CPE content the higher is the pPVC/CPEs Tg values. Moreover, comparing the samples containing the same amount of the three different CPEs, higher Tg values are shown when CPE3680 and CPE6135A are added to pPVC. This finding can be explained in terms of CPE chlorine content.

Probably, the higher is the CPE chlorine content the greater is its interaction with PVC, reducing the polymer chains mobility thus increasing the Tg of the blends.

The Young's modulus (E), ultimate tensile strength (σ_b) and elongation at break (ε_b) of pPVC and its blends with CPEs are also reported in table 22.

It can be seen that all the pPVC/CPEs blends underwent break at lower stresses and elongations than pPVC. Moreover, both stress and strain at break slightly decrease with increasing CPE content.

This finding is in agreement with DMA results confirming the CPE hardening effect on flexible PVC compounds. Absorbing the plasticizer, CPE is able to reduce the plasticization efficiency of DOP in PVC thus affecting the pPVC mechanical properties.

Sample	Tg (°C)	E (MPa)	ε_b (%)	σ_b (MPa)
pPVC	11	6.73 ± 0.5	289.78 ± 11.12	9.38 ± 1.8
PVC/CPE252 (7%)	17	6,67 ± 0.09	242.35 ± 13.84	7.202 ± 0.44
PVC/CPE252 (15%)	19	7,28 ± 0.1	228.71 ±15.70	4.92 ± 0.36
PVC/CPE3680 (7%)	22	7,00 ± 0.1	268.58 ± 16.7	8.82 ± 0.36
PVC/CPE3680(15%)	26	7,67 ± 0.1	205.29± 13.48	5.99 ± 0.36
PVC/CPE6135A (7%)	21	7,28 ± 0.1	288.71 ± 19.60	7.32 ± 0.95
PVC/CPE6135A (15%)	27	7,86 ± 0.2	204.37 ± 8.61	5.66 ± 0.34

Table 22. Mechanical and dynamic-mechanical results.

6.3.3 Migration tests

Migration tests were performed, for 30 days, in order to verify the efficiency of CPE as a barrier to DOP migration.

The weight loss (negative) versus time of pPVC/CPE blends containing 7 wt% (figure 37) and 15 wt% (figure 38) of CPEs are shown.

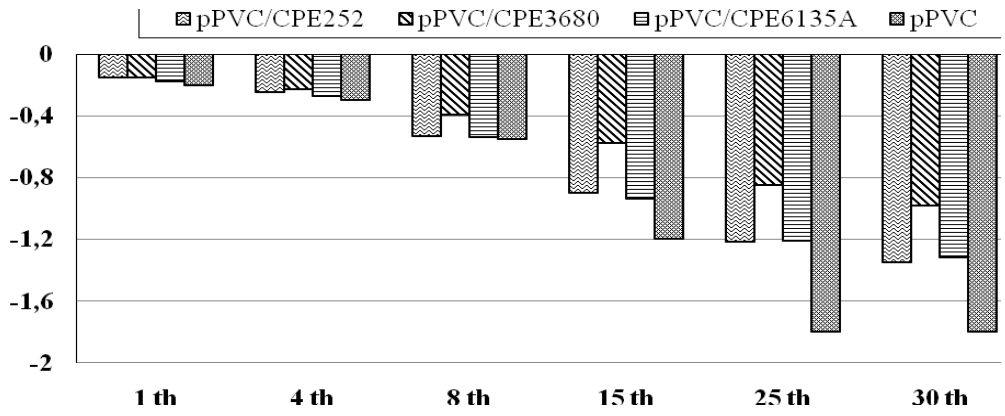

Figure 37. The weight loss versus time of pPVC/CPE blends containing 7 wt% of CPEs.

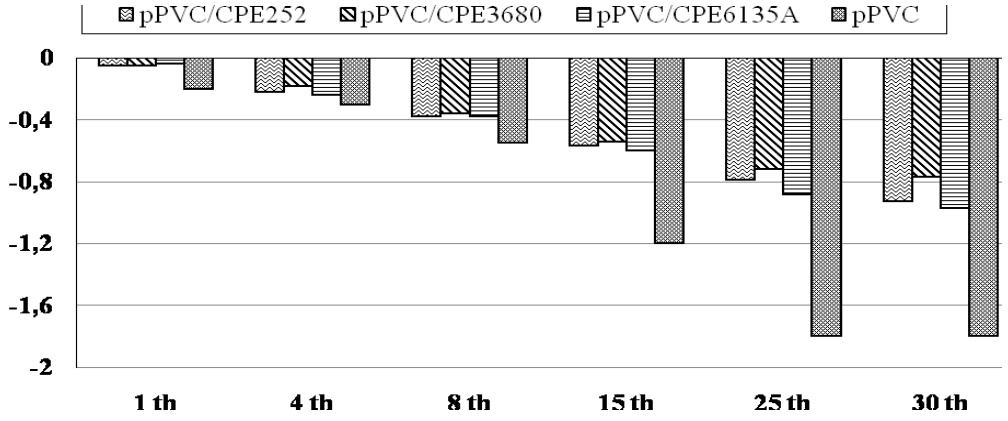

Figure 38. The weight loss versus time of pPVC/CPE blends containing 15 wt% of CPEs.

It can be noted that CPE acts as physical barrier against DOP migration, since all the pPVC/CPEs blends weight loss over time is lower compared with pPVC. This behavior can be ascribed to the good solubility of CPEs in DOP. CPE is able to absorb the DOP hampering its release. Moreover, when CPE content is higher, DOP migration is hindered more efficiently. The blends containing CPE3680, at any concentrations, showed the lowest values of weight loss over time. The differences in barrier ability against DOP migration in the three types of CPE can be explained in terms of chlorine percentage. Probably, the higher is the CPE chlorine content the greater is its interaction with sPVC reducing the free volume and consequently the DOP migration [18].

6.3.4 Tribological analysis

The friction coefficient, or simply friction, is a measure of the sliding resistance of a surface in contact with another. The friction expresses the "slip", which depends basically on the chemical nature of the material and the presence of additives which may promote it (sleep agents) or hinder it (anti-sleep agents). The materials behavior to friction is influenced by the microstructure of the surface layer. The distribution of the phases and the hardness of individual phases are very important factors to be considered.

Therefore, by tribological tests it is possible to have an indirect measurement of the CPE barrier effect on the DOP migration. The plasticizer motion towards the material surface layer should increase the adhesion, between the pin and the sample surface, leading to increased friction coefficient values. On the contrary it should be noted decreased friction values.

The tribological properties of pPVC/CPEs blends were studied.

The dynamic friction coefficients are shown in figure 39-41, as a function of the number of revolutions, for pPVC/CPEs blends containing the three different CPEs at 7 and 15% by weight compared with rigid PVC (uPVC) and flexible PVC (pPVC) samples.

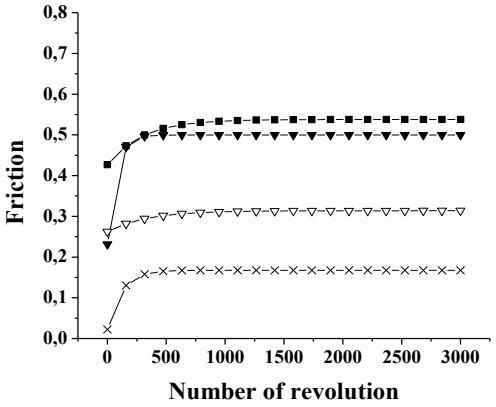

Figure 39. Friction behavior for uPVC (-×-), pPVC (-■-), pPVC/CPE3680(7%) (-▼-), pPVC/CPE3680(15%) (-◪-).

Samples containing 15 wt% of CPEs are characterized by a friction coefficient values much closer to that of rigid PVC since the DOP diffusivity was much more hindered as demonstrated by migration tests results.

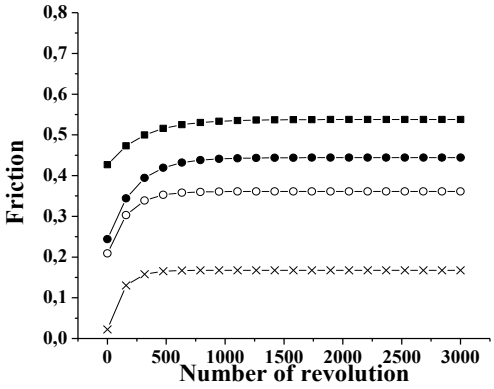

Figure 40. Friction behavior for uPVC (-×-), pPVC (-■-), pPVC/CPE6135A(7%) (-●-), pPVC/CPE6135A(15%) (-○-).

In the case of pPVC blends containing 7 wt% of CPEs the DOP migration was less hindered and the friction coefficient values are much closer to that of flexible PVC (pPVC). This finding is a further evidence of the effectiveness of CPE as a physical barrier to DOP migration. The higher the CPEs content the greater is the plasticizer retention.

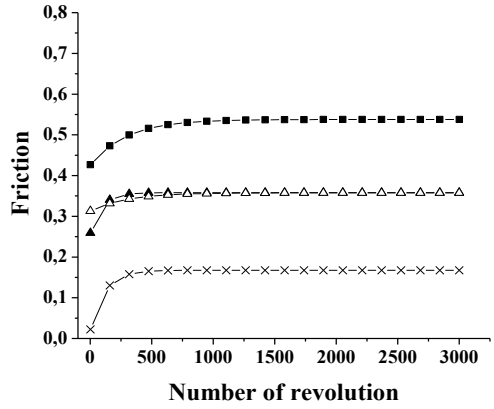

Figure 41. Friction behavior for uPVC (-×-), pPVC (-■-), pPVC/CPE252(7%) (-▲-), pPVC/CPE252(15%) (-▲-).

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CHAPTER 7

Conclusions

Polyvinyl chloride is characterized by a very wide range of properties which explain its use in many applications. However, PVC itself is hard and rigid, and in order to achieve good properties it requires the use of additives during the manufacturing process. The additives which may be loaded to the polymer are numerous and are distinguished by the characteristics which they provide to the material. Plasticizer plays a major role making the polymer soft and flexible.
There are several possible classifications justified by variability of the chemical structure, features, range of use and efficiency PVC plasticizers. It is proper to make a division based on the plasticizers chemical nature, namely the functional groups and molecular morphology characterizing the plasticizers themselves. However, in this work, we have made a classification on the bases of plasticizer molecular weight, that is:

- *monomeric plasticizers,* which are low molecular weight compounds
- *polymeric plasticizers,* which are polymers with higher average molecular weights.

Phthalates, phosphates, trimellitates, citrates, sebacates and adipates are the most common momomeric as plasticizers used for PVC. Since they are not chemically bonded with the polymer matrix and because of their low molecular weights, monomeric plasticizers have a high tendency to leach out from the polymer thus representing a serious problem for applications.
In particular, the use of phthalate-based plasticizers is being questioned worldwide because of their potential toxicity to humans and environment. Additionally, when rigid and flexible PVC are co-extruded as in the case of spiral pipes, if the plasticizer diffusion extent is not controlled or reduced the Environmental Stress Cracking (ESC) phenomena may occur. This is a solvent-induced failure mode, in which the synergistic effects of the chemical agent and mechanical stresses result in cracking causing the materials failure in service.
Aim of this PhD work has been to investigate several approaches devoted to limiting the plasticizer migration.
The first strategy was *the chemical cross-linking* of PVC macromolecules, using the difunctional ammine IPDA as cross-linking agent in different amount. The efficiency of IPDA as a chemical cross-linker for PVC was evaluated by means of solvent extraction procedure, weighting the gelled portion insoluble in THF. It was found that the higher was the percentage of cross-linker used, the higher was the insoluble fraction of PVC, as a consequence of the chemical cross-linking reaction promoted by IPDA. Nevertheless, considering the thermal stability of the materials, it is likely that the increased concentration of HCl due to the use of IPDA is

responsible for faster degradation of PVC. The decrease of molecular weight of PVC macromolecules upon thermal degradation during the processing is confirmed also by the glass transition temperatures of soft cross-linked samples, which were lower in comparison with that of pPVC. The most important parameter to be considered for evaluating the effect of cross-linking on the plasticizer migration extent was the percentage weight variations determined for rigid PVC sheets kept in contact with plasticized samples. After 30 days, the weight increase of rigid PVC sheets was about 18 % lower than that of sheets in contact with pPVC sample. In fact, the formation of more chemical bonds reduced the free volume and segmental macromolecules mobility, thus affecting plasticizer diffusion through the matrix. This finding proved that PVC chemical cross-linking could be an attractive tool to overcome the disadvantage related to the plasticizer migration. Nevertheless, the amount of DOP migrating from cross-linked samples turned out to be independent of the cross-linker loading.

Another option for achieving significant inhibition of plasticizer migration and minimization of property deterioration has been the blending of PVC with a polymeric plasticizer. Linear polymeric plasticizers are employed as an alternative or in addition to the usual monomeric plasticizers to provide flexibility, softness and lower modulus values and to maintain these characteristics after PVC compound exposure to severe use conditions or harsh environments.
Because of their higher molecular weight and bulkiness their volatility and diffusivity is reduced compared with monomeric plasticizers. On the other hand, their use usually makes the material more difficult to process. Therefore, a manufacturing dilemma is to select the right molecular weight to use in order to satisfy the conflicting requirements of increased plasticizer retention and decreased manufacturing compatibility and processibility. In the recent years, a growing interest has been shown also for more complex polymer architectures (namely hyperbranched polymers) as substitute to phthalate plasticizers for PVC. In comparison with analogue linear polymers, their compact structure, the absence of chain entanglements, and presence of a large number of functional end groups enable a spectrum of unusual properties and consequently numerous possible applications. As discussed in the literature, the variations in many of hyper-branched polymers properties are related to their different degree of branching. In this work the hyper-branched poly(butylene adipate) (HPBA) was synthesized according to the procedure reported by Linstrom et. al. Then PVC blends based on linear and hyper-branched polymers

were used prepared. The properties of PVC/polymeric plasticizers blends were studied and compared with those of PVC/DOP (pPVC) formulation.

The ^{1}H NMR spectrum of hyper-branched polyester revealed the occurrence of the trans-esterification reaction of 1,4 butanediol and dimethyl adipate monomers, leading to the formation of poly(butylene adipate) oligomers in the first step of the synthesis. In the second step, the addition of TMP leads to formation of the hyper-branched structure evidenced by the chemical shift of the cross-linking agent signals.

Thermal, morphological, mechanical and migration tests were performed on PVC/polymer plasticized blends. Since HPBA and Palamoll were basically more stable upon heating, their presence in PVC increased blends thermal stability by about 40 °C, regardless of the polyesters amount used. WAXD was carried out to investigate the morphology of PVC/HPBA blends and any signal related to the HPBA crystallinity was detected, meaning that HPBA looses its structure when added to PVC. The blends resulted amorphus at any PVC/HPBA ratio indicating good miscibility between the polymers. The analogous information derived from the evaluation of glass transition temperatures, since a single value was observed at each composition. The high miscibility between polyester and PVC is due to the hydrogen bonding between the carbonyl group of the ester and the α-hydrogen next to the chlorine atom in PVC. Moreover, monotonic shift of transition temperatures toward low values were observed with addition of polymeric plasticizers. Comparing the samples containing the same amount of plasticizer, both linear and hyper-branched, each PVC-HPBA based system showed a T_g value of about ten degrees higher than the corresponding PVC-Palamoll based blend and pPVC. This was probably due to the complex architecture of HPBA which restricted the PVC macromolecules chain mobility.

As for migration tendency, the polymeric plasticizers were expected to have better migration stability compared to the monomeric ones. The weight loss of the exudable flexible component was determined by measuring the weights of the samples at different aging times, i.e t =1, 4, 8, 15, 25 and 30 days. As expected, HPBA containing system exhibited the lowest values of weight loss, which remain constant with the aging time, meaning that an efficient plasticizer retention was achieved by the use of highly branched poly(butylene adipate).

The last strategy adopted in this work regarded the addition of chlorinated polyethylene (CPE) to pPVC formulations. Chlorinated polyethylene (CPE) represent an important class of commercial

polymers. CPE resin is mainly used in blends with other polymers to improve their mechanical properties, as compatibilizer in polymer blends or as base thermoplastics for extruded, calendered, solution cast and injection-moulded parts and goods.

Of particular importance is the use of chlorinated polyethylene (CPE) as a high-molecular weight plasticizer for improving the physico-mechanical characteristics of un-plasticized PVC (uPVC). CPE is non-volatile, and does not migrate in blends with PVC, therefore, the plasticized composition have a considerably higher service life. The addition of CPE to uPVC raises its impact strength and fire resistance, reducing the brittle point.

In this work CPE was used, in flexible PVC, as a physical tool to create a barrier against DOP migration thanks to its ability to absorb the plasticizer. Three different CPEs, having different viscosity and chlorine content, were added in 7 and 15% by weight in flexible PVC.

The properties of pPVC/CPEs blends were studied and compared with those of pPVC formulation. Thermal, mechanical, tribological and migration tests were performed on pPVC/CPEs blends. Since CPE is more thermally stable compared to PVC, its addition in pPVC formulation slightly increased blends thermal stability by about 10 °C, regardless of the CPEs amount used.

As for migration tests it was noted that CPE acts as efficient physical barrier against DOP migration. This behavior can be ascribed to the good solubility of CPEs in DOP. Moreover, when CPE content was higher, DOP migration was hindered more efficiently. The differences in barrier ability against DOP migration in the three types of CPE can be explained in terms of chlorine percentage. Probably, the higher was the CPE chlorine content the greater was its interaction with PVC reducing the free volume and consequently the DOP migration. Tribological characterization was a further evidence of the effectiveness of CPE as a physical barrier to DOP migration. In general, the higher the CPEs content the greater was the plasticizer retention. In fact, samples containing 15 wt% of CPE were characterized by a friction coefficient values much closer to that of rigid PVC since the DOP diffusivity was much more hindered. According to the obtained results the three approaches proposed are effective to reduce the potential health risk related to the migration of DOP from the PVC matrix.

Loss of plasticizer was limited by the cross-linking of the PVC matrix, the use of synthetic HPBA and the physical barrier represented by CPE, without affecting the final properties of flexible PVC products.